

## **Supporting Information**

### **Bismuth-Catalyzed Oxidative Coupling of Arylboronic Acids with Triflate and Nonaflate Salts**

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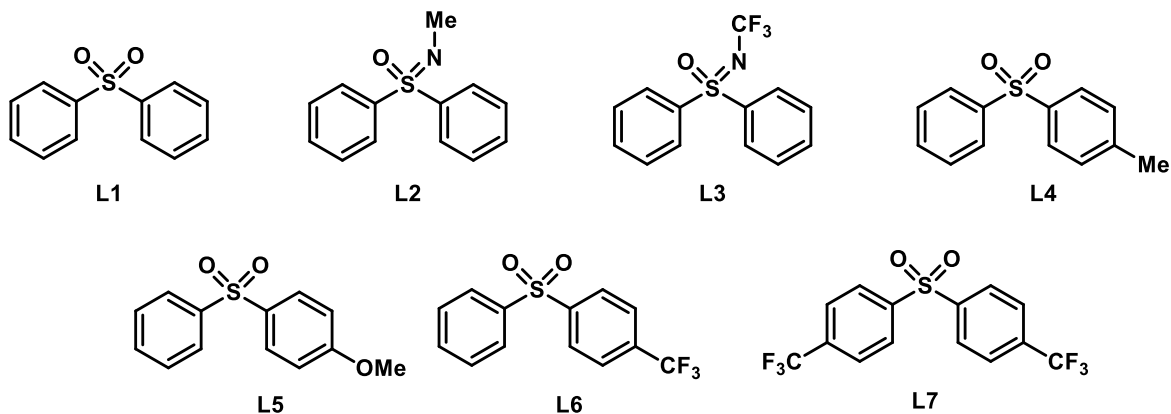
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## 1. General methods

### 1.1 Experimental methods

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under dry argon (Ar) in flame-dried glassware. Anhydrous solvents were distilled from appropriate drying agents and were transferred under Ar: tetrahydrofuran (Na/K), chloroform (CaH<sub>2</sub>) and chloroform-*d* (MS), acetonitrile (SPS) and acetonitrile-*d*<sub>3</sub> (MS), acetone, toluene (Na/K), dichloromethane (CaH<sub>2</sub>/P<sub>4</sub>O<sub>10</sub>) and dimethylformamide (MS). Commercially available xenon difluoride obtained from STREM, 1-fluoro-2,6-dichloropyridinium tetrafluoroborate, 1-fluoro-2,6-dichloropyridinium triflate, sodium triflate, potassium nonaflate and all the arylboronic acids utilized in this work were obtained from Sigma-Aldrich. Molecular sieves were dried at 250 °C for 2 days before use. Flash chromatography: Merck silica gel 60 (40-63 μm). ESI-MS: ESQ 3000 (Bruker). Preparative TLC plates: PLC Silica gel 60 F<sub>254</sub>, 1 mm, 20x20 cm (Sigma-Aldrich). High-resolution mass determinations: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan). NMR spectra were recorded using 300 MHz Bruker Avance III and 500 MHz Bruker Avance III NMR spectrometers. <sup>1</sup>H NMR spectra (300.13 MHz, 500.1 Hz) were referenced to the residual protons of the deuterated solvent,<sup>1</sup> and are reported to tetramethylsilane ( $\delta_{\text{TMS}} = 0$  ppm), chloroform-*d* ( $\delta_{\text{TMS}} = 7.26$  ppm) or acetonitrile-*d*<sub>3</sub> ( $\delta_{\text{TMS}} = 1.94$  ppm). <sup>13</sup>C{<sup>1</sup>H} NMR spectra (75.47 MHz, 125 MHz) were referenced internally to the D-coupled <sup>13</sup>C resonances of the NMR solvent and are reported to tetramethylsilane ( $\delta_{\text{TMS}} = 0$  ppm), chloroform-*d* ( $\delta_{\text{TMS}} = 77.16$  ppm) or acetonitrile-*d*<sub>3</sub> ( $\delta_{\text{TMS}} = 1.32$  ppm). <sup>19</sup>F{<sup>1</sup>H} NMR spectra (282 MHz, 471 MHz) are reported relative to the <sup>19</sup>F resonances of CFCl<sub>3</sub>. Chemical shifts ( $\delta$ ) are given in ppm, relative to deuterated solvent residual peak, and coupling constants (*J*) provided in Hz. For aryl nonaflates **5a-e** and bismine nonaflate **4d**, <sup>13</sup>C NMR spectra were acquired with a Bruker BB-1H/19F TBO Probe with inverse gated decoupling. For <sup>1</sup>H NMR waltz16 was used for decoupling. For <sup>19</sup>F the decoupling scheme bi\_p5m4sp\_4sp.2 with adiabatic chirp pulses was used to ensure the broadband decoupling on <sup>19</sup>F. Sometime small artifacts can be seen in the spectra. <sup>19</sup>F-HMQCs were acquired to show which <sup>19</sup>F signals correlate with the corresponding <sup>13</sup>C nuclei.

## 2. Synthesis of ligands

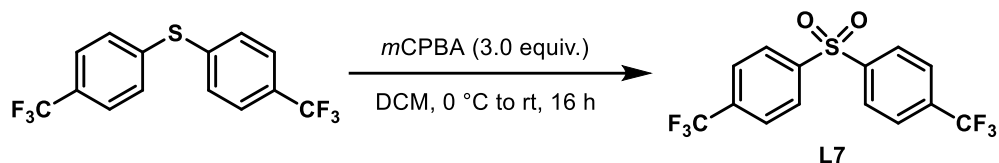


**Figure S1.** Ligands utilized in this study.

Ligand **L1**,<sup>2</sup> **L2**,<sup>3</sup> **L3**<sup>4</sup> and **L4**<sup>2</sup> were synthesized following previously reported protocols. Ligands **L5** and **L6** were synthesized by oxidation of the corresponding thioether<sup>5</sup> with *meta*-chloroperbenzoic acid (*m*CPBA).<sup>6</sup> Characterization and spectroscopic data for all of them matches those described in the literature. Ligand **L7** was synthesized using the same protocol, which is described below.



## 2.1 Synthesis of diarylsulfone ligand **L7**



A round bottomed flask equipped with a stir bar was charged with bis(4-(trifluoromethyl)phenyl)sulfane<sup>7</sup> (2.3 g, 7.1 mmol, 1.0 equiv.) and 20 mL of CH<sub>2</sub>Cl<sub>2</sub> under air. The reaction mixture was cooled to 0 °C, and *m*CPBA (3.7 g, 21.4 mmol, 3.0 equiv.) was added in portions as a solid. The reaction is stirred overnight slowly warming to room temperature. Then, a solution of saturated Na<sub>2</sub>CO<sub>3</sub> was added slowly (vigorous CO<sub>2</sub> evolution) and the resulting mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 × 50 mL). The combined organics were dried over Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to give **L7** as a white solid (2.245 g, 6.3 mmol, 89%). The product obtained was used without further purification.

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 8.09 (d, *J* = 8.1 Hz, 4H), 7.80 (d, *J* = 8.1 Hz, 4H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 144.3, 135.6 (q, *J* = 32.9 Hz), 128.6, 126.4 (q, *J* = 3.6 Hz), 123.1 (q, *J* = 272.9 Hz).

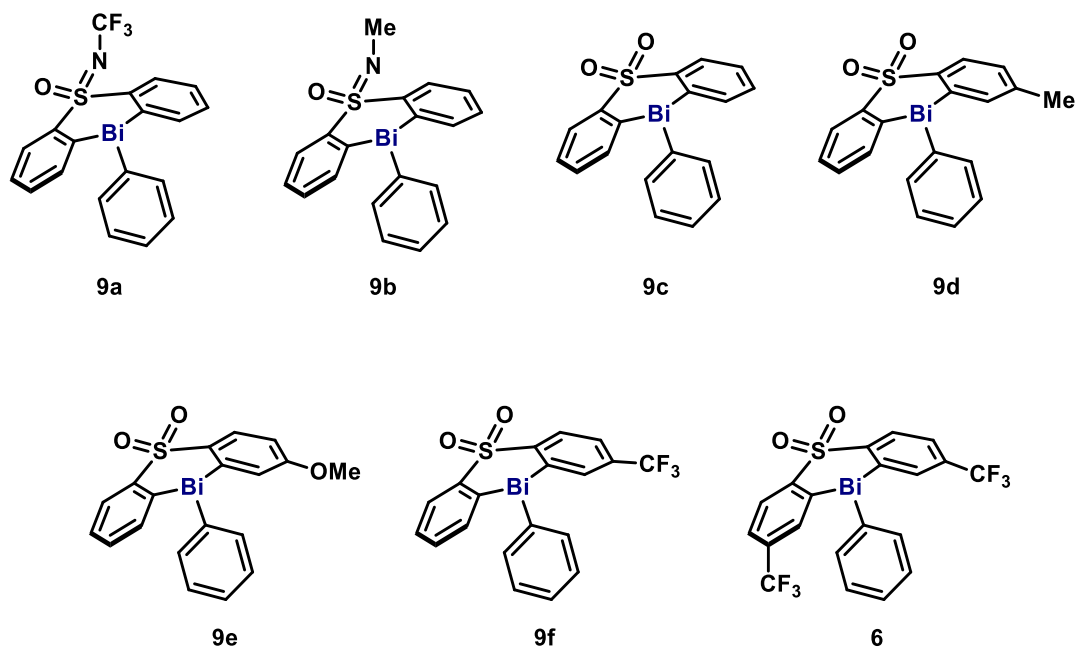
**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -63.4 (s, 6F).

**HRMS (EI, m/z)**: calc'd for C<sub>14</sub>H<sub>8</sub>O<sub>2</sub>S<sub>1</sub>F<sub>6</sub> [M]<sup>+</sup> 354.0144; found 354.0146.

**m.p. (°C)**: 141.5 – 142.3.

### 3. Synthesis of Bi(III) compounds

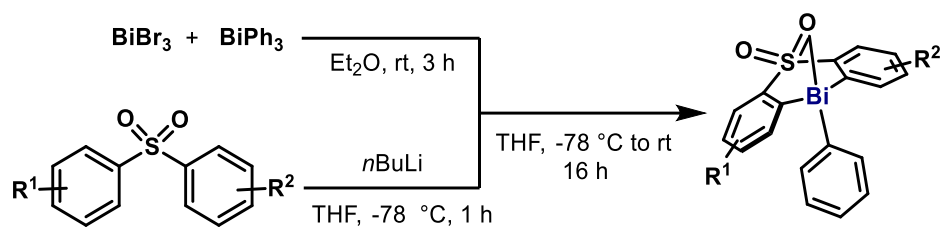
#### 3.1 Synthesis of phenylbismines



**Figure S2.** Phenylbismines synthesized.

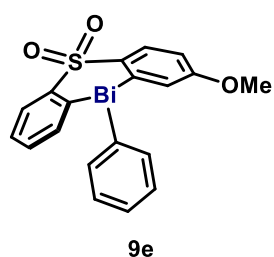
Phenylbismines **9a-d** were synthesized according to a previously reported protocol.<sup>8</sup> Phenylbismines **9e**, **9f** and **6** were synthesized following the procedure described below.

General procedure for the synthesis of phenylbismines.<sup>9</sup>



A Schlenk flask equipped with a stir bar was charged with  $BiBr_3$  (0.66 equiv.),  $BiPh_3$  (0.33 equiv.) and  $Et_2O$  (8 mL) under an Ar atmosphere and stirred at room temperature for 3 h. THF (10 mL) was added to completely dissolve the yellow precipitate, and this solution was added dropwise to a  $-78\text{ }^\circ\text{C}$  dilithiated ligand solution. The dilithiated ligand was prepared in a separate Schlenk flask from the corresponding ligand (1 equiv.), dissolved in THF (30 mL), with *n*-butyllithium (2.6 M in hexanes, 2.1 equiv.) at  $-78\text{ }^\circ\text{C}$  for 1 h. Following the addition of the bismuth compound to the dilithiated ligand, the reaction was stirred overnight, slowly warming to room temperature. The reaction was quenched by the addition of brine (20 mL), extracted with  $EtOAc$  (40 mL), and re-extracted with  $CH_2Cl_2$  ( $2 \times 50\text{ mL}$ ). The combined organics were dried over  $Na_2SO_4$ , filtered and concentrated to give a thick yellow residue. The crude material was purified by flash chromatography (silica gel, hexanes/ $EtOAc$ ) to give the corresponding phenylbismine as a white solid.

**2-Methoxy-10-phenyl-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (9e):** Following the



general procedure, using 2.2 g of **L5** as ligand, **9e** was obtained in 53% yield as a white solid (Eluent: hexanes/EtOAc = 4/1).

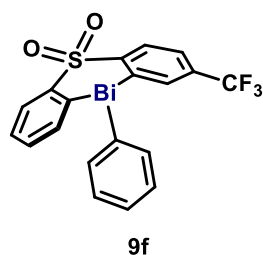
**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 8.36-8.30 (m, 2H), 7.85 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.86-7.80 (m, 2H), 7.46-7.29 (m, 6H), 6.85 (dd, *J* = 8.6, 2.4 Hz, 1H), 3.68 (s, 3H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 166.2, 163.6, 160.5, 158.4, 142.7, 138.8, 137.6, 133.3, 133.2, 131.0, 129.1, 128.7, 128.2, 126.7, 123.5, 112.9, 55.6.

**HRMS (ESI, *m/z*):** calc'd for C<sub>19</sub>H<sub>15</sub>BiSO<sub>3</sub>Na<sup>+</sup> [*M*+Na]<sup>+</sup> 555.04379; found 555.04379.

**m.p. (°C):** 144.7 – 145.9.

**10-Phenyl-2-(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (9f):** Following



the general procedure using 1.1 g of **L6** as ligand, **9f** was obtained in 50% yield as a white solid (Eluent: hexanes/EtOAc = 4/1).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 8.47 (d, *J* = 8.2 Hz, 1H), 8.40 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.09 (s, 1H), 7.77 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.76 (m, 2H), 7.68 (dd, *J* = 8.1, 1.8 Hz, 1H), 7.50-7.36 (m, 5H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 166.6, 166.5, 159.6, 145.5, 141.1, 138.7, 137.8, 134.8 (q, *J* = 32.6 Hz), 134.5 (q, *J* = 3.6 Hz), 134.0, 131.3, 129.2, 128.6, 127.8, 127.2, 135.5 (q, *J* = 3.6 Hz), 123.3 (q, *J* = 272.9 Hz).

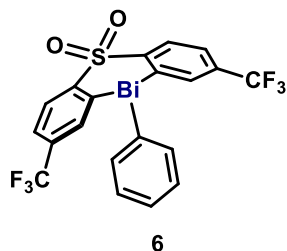
**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -62.9 (s, 3F).

**HRMS (ESI, *m/z*):** calc'd for C<sub>19</sub>H<sub>12</sub>BiF<sub>3</sub>SO<sub>2</sub>Na<sup>+</sup> [*M*+Na]<sup>+</sup> 593.0206; found 593.0204.

**m.p. (°C):** 173.0– 173.9.

**10-Phenyl-2,8-bis(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine 5,5-dioxide (6):**

Following the general procedure, using 2.2 g of **L7** as ligand, **6** was obtained in 22% yield as white solid (Eluent: hexanes/EtOAc = 4/1).



**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 8.48 (d, *J* = 8.0 Hz, 2H), 8.12 (s, 2H), 7.76 (d, *J* = 7.9, 1.6 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.54-7.41 (m, 3H).

**<sup>13</sup>C NMR** - (101 MHz, CDCl<sub>3</sub>): δ 167.2, 160.6, 144.7, 138.6, 135.4 (q, *J* = 32.7 Hz), 134.7 (q, *J* = 3.7 Hz), 131.7, 129.6, 127.7, 125.8 (q, *J* = 3.8 Hz), 123.2 (q, *J* = 272.3 Hz).

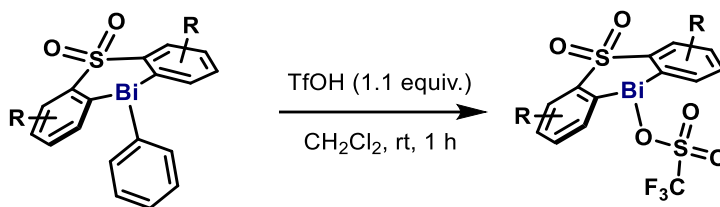
**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -63.0 (s, 3F).

**HRMS (ESI, m/z):** calc'd for C<sub>20</sub>H<sub>11</sub>BiF<sub>6</sub>SO<sub>2</sub>Na<sup>+</sup> [M+Na]<sup>+</sup> 661.0080; found 661.0076.

**m.p. (°C):** 81.1 – 82.6.

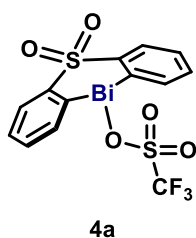
### 3.2 Synthesis of bismine triflates

Bismine triflates were synthesized following a previously reported method.<sup>10</sup>



General procedure: Phenylbismine (1.0 equiv.) was mixed with CH<sub>2</sub>Cl<sub>2</sub> and trifluoromethanesulfonic acid (1.1 equiv.) and the reaction was stirred for 1 h at room temperature. Then, the solvent was removed under vacuum, and the remaining solid was washed with a CH<sub>2</sub>Cl<sub>2</sub>/pentane (1:5) solution. The white solid was dried under vacuum for 1 h.

#### 5,5-Dioxido-10H-dibenzo[b,e][1,4]thiabismine-10-yl trifluoromethanesulfonate (**4a**):



Following the general procedure, using 126 mg of **6**, **4a** was obtained in 91% yield as a white solid. Characterization was consistent with the previously reported data for this compound.<sup>10</sup>

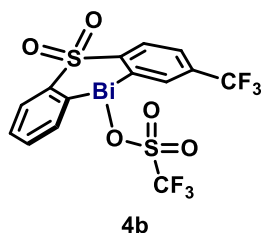
**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 9.00 (dd, *J* = 7.6, 1.1 Hz, 2H), 8.47 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.92 (td, *J* = 7.6, 1.2 Hz, 2H), 7.56 (td, *J* = 7.6, 1.1 Hz, 2H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 191.4, 139.0, 137.1, 135.3, 130.2, 129.6, 118.9 (q, *J* = 320.7 Hz).

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ 76.9 (s, 3F).

**HRMS (ESI, *m/z*):** calc'd for C<sub>13</sub>H<sub>8</sub>BiF<sub>3</sub>SO<sub>5</sub>Na<sup>+</sup> [*M*+Na]<sup>+</sup> 596.9461; found 596.9463.

**5,5-Dioxido-2-(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine-10-yl**



**trifluoromethanesulfonate (4b):** Following the general procedure starting from 114 mg of **9f**, **4b** was obtained in 94% yield as white solid.

**<sup>1</sup>H NMR** - (300 MHz, CD<sub>3</sub>CN): δ 9.35 (s, 1H), 9.13 (d, *J* = 7.5 Hz, 1H), 8.59 (d, *J* = 7.5 Hz, 1H), 8.53 (dd, *J* = 7.7, 0.8 Hz, 1H), 8.01 (td, *J* = 7.7, 1.1 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.63c (td, *J* = 7.7, 1.2 Hz, 1H)

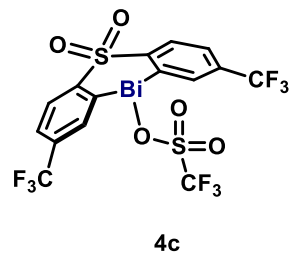
**<sup>13</sup>C NMR** - (75 MHz, CD<sub>3</sub>CN): δ 201.2, 200.9, 144.8, 139.9, 138.4, 138.1 (q, *J* = 32.6 Hz), 136.5, 133.2 (q, *J* = 3.8 Hz), 131.3, 131.0, 130.4, 127.4 (q, *J* = 3.8 Hz), 124.8 (q, *J* = 272.8 Hz), 121.1 (q, *J* = 242.7 Hz)

**<sup>19</sup>F NMR** - (282 MHz, CD<sub>3</sub>CN): δ -63.5 (s, 3F), -78.6 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>14</sub>H<sub>7</sub>BiO<sub>5</sub>S<sub>2</sub>F<sub>6</sub> [M]<sup>+</sup> 641.9443; found 641.9453.

**m.p. (°C):** 198.9 – 200.0.

**5,5-Dioxido-2,8-bis(trifluoromethyl)-10H-dibenzo[b,e][1,4]thiabismine-10-yl**



obtained in 98% yield as white solid.

**<sup>1</sup>H NMR** - (300 MHz, CD<sub>3</sub>CN): δ 9.40 (s, 2H), 8.63 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 8.1 Hz, 2H).

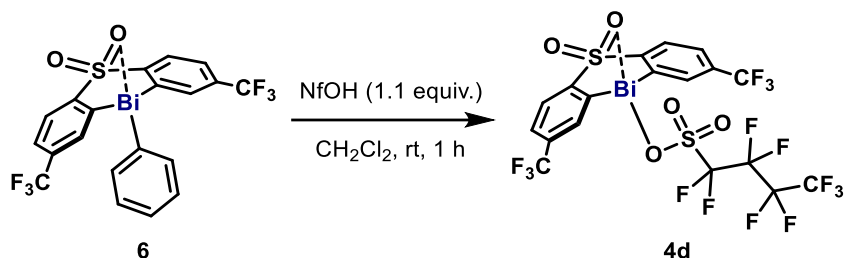
**<sup>13</sup>C NMR** - (75 MHz, CD<sub>3</sub>CN): δ 203.4, 144.2, 138.4 (q, *J* = 32.7 Hz), 133.5 (q, *J* = 3.7 Hz), 131.6, 127.5 (q, *J* = 3.7 Hz), 125.1 (q, *J* = 272.7 Hz), 121.1 (q, *J* = 242.7 Hz).

**<sup>19</sup>F NMR** - (282 MHz, CD<sub>3</sub>CN): δ -63.6 (s, 6F), 78.8 (s, 3F).

**HRMS (ESI, m/z):** calc'd for C<sub>15</sub>H<sub>6</sub>BiF<sub>9</sub>S<sub>2</sub>O<sub>5</sub>Na<sup>+</sup> [M+Na]<sup>+</sup> 732.9205; found 732.9209.

**m.p. (°C):** 235.0 – 235.9.

### 3.3 Synthesis of bismine nonaflate **4d**



Bismine nonaflate **4d** was synthesized following the same method utilized for the synthesis of bismine triflates (see section 3.2). Phenylbismine **6** (191 mg, 0.3 mmol, 1.0 equiv.) was mixed with CH<sub>2</sub>Cl<sub>2</sub> (2 mL) and nonafluorobutane-1-sulfonic acid (55  $\mu$ L, 1.1 equiv.) and the reaction was stirred for 1 h at room temperature. Then, the solvent was removed, and the remaining solid was washed with a CH<sub>2</sub>Cl<sub>2</sub>/pentane (1:5) solution. The white solid was dried under vacuum for 1 h, obtaining 235 mg of the title compound (91%).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>):  $\delta$  9.34 (s, 2H), 8.61 (d,  $J$  = 8.1 Hz, 2H), 7.86 (dd,  $J$  = 7.9, 1.7 Hz, 2H).

**<sup>13</sup>C {<sup>19</sup>F} NMR** - (75 MHz, CDCl<sub>3</sub>):  $\delta$  194.9, 142.0, 139.1, 132.9, 130.8, 127.2, 123.4, 117.3, 113.4, 110.4, 108.7.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>):  $\delta$  -63.3 (s, 6F), -80.9 (s, 3F), -112.5– -112.6 (m, 2F), -121.2– -121.3 (m, 2F), -126.0– -126.1 (m, 2F).

**HRMS (ESI, m/z)**: calc'd for C<sub>18</sub>H<sub>6</sub>BiF<sub>15</sub>S<sub>2</sub>O<sub>5</sub>Na<sup>+</sup> [M+Na]<sup>+</sup> 882.9113; found 882.9110.

**m.p. (°C)**: 178.5 – 179.8.

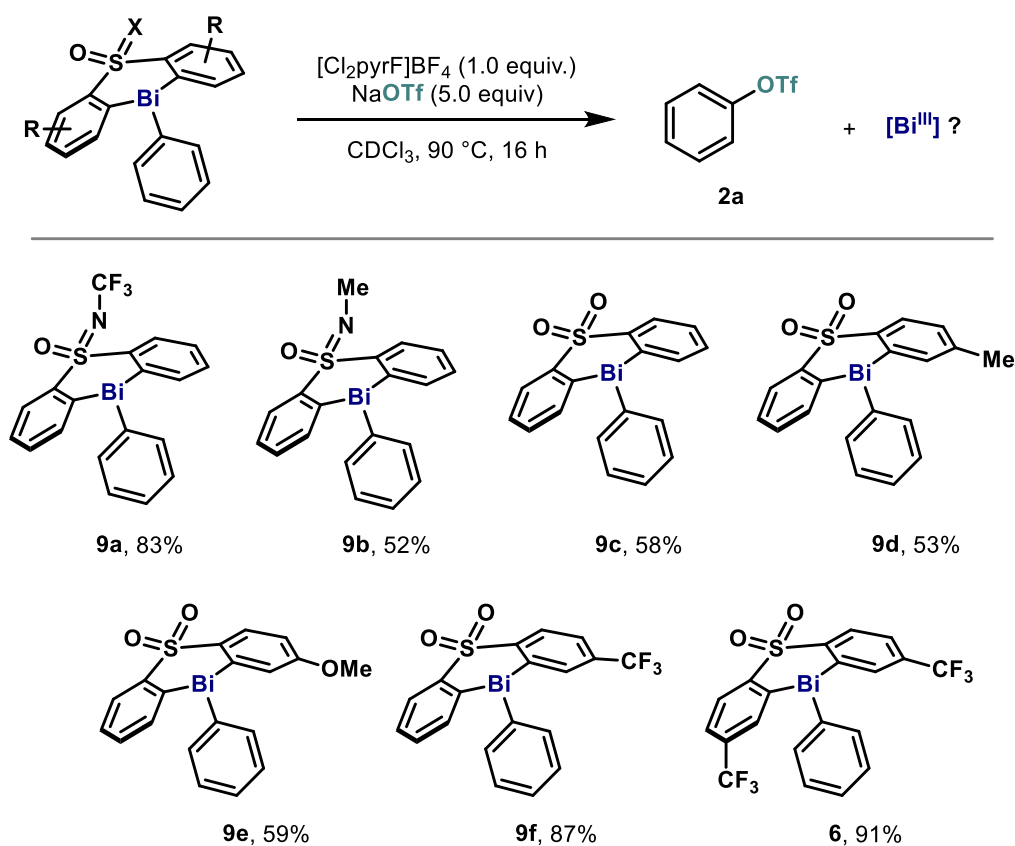


## 4. Stoichiometric studies

### 4.1 Optimization of ligand backbone

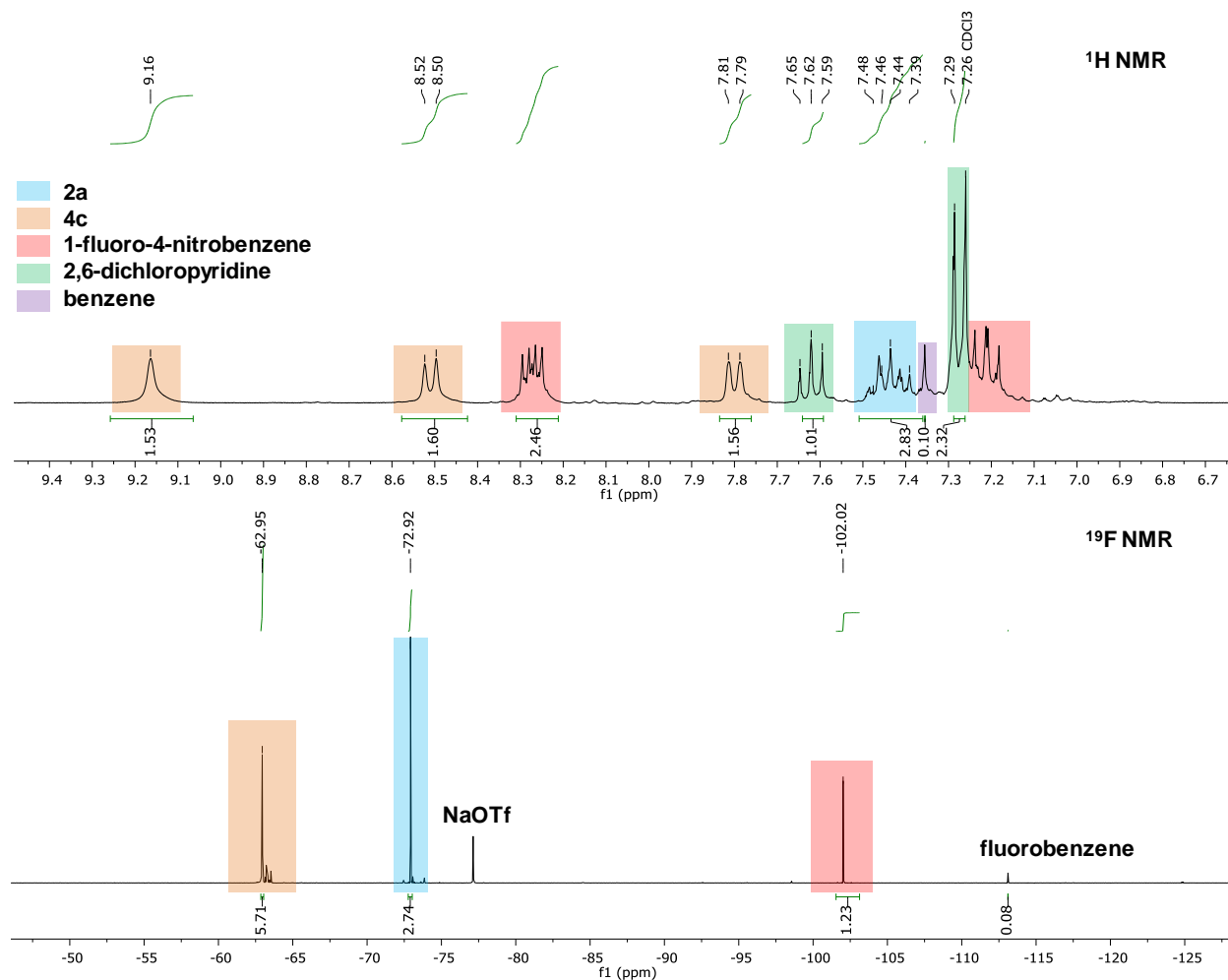
The corresponding phenylbismine (0.025 mmol), 1-fluoro-2,6-pyridinium tetrafluoroborate (7.6 mg, 0.03 mmol) and sodium triflate (21.5 mg, 0.125 mmol) were mixed with CDCl<sub>3</sub> (1 mL) under an Ar atmosphere and the reaction was stirred for 16 h at 90 °C. Then, 1-fluoro-4-nitrobenzene was added as internal standard (0.025 mmol, addition by weight) and the crude reactions were analyzed by <sup>19</sup>F NMR to determine the yield of aryl triflate.

**Table S1.** Optimization of the ligand backbone for the obtention of phenyl triflate **2a** from phenylbismines and 1-fluoro-2,6-pyridinium tetrafluoroborate.



As shown in Table 1, bismine containing CF<sub>3</sub> groups furnished **2a** in high yields after the oxidation-reductive elimination sequence. Although **9a** also generated **2a** in good yields, it was partially decomposed after reaction completion, and a significant amount of benzene was detected (>10%). On the other hand, when **6** was oxidized in presence of NaOTf at 90 °C, an excellent yield

of **2a** was obtained, together with the corresponding Bi(III)-OTf (**4c**) and trace amounts of benzene (Figure S3). Similar results were obtained with **9f**.



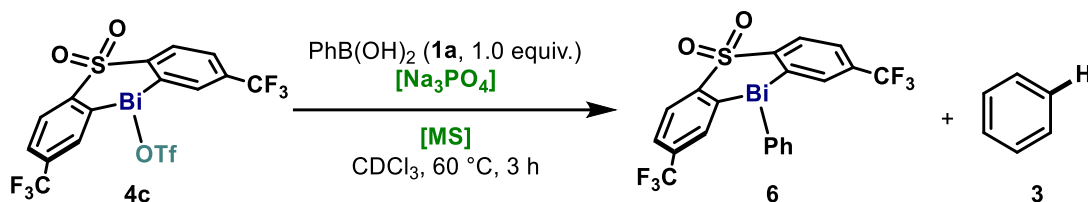
**Figure S3.** <sup>1</sup>H NMR (top) and <sup>19</sup>F NMR (bottom) analysis of the reaction crude after the oxidation-reductive elimination sequence with **6** using 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (1.0 equiv.) and NaOTf (5.0 equiv.) in CDCl<sub>3</sub> at 90 °C.

Based on these results, the corresponding triflates of **9f** and **6** (**4b** and **4c**, respectively) were synthesized to be tested in the catalytic reaction, together with the corresponding triflate of **9c** (**4a**) as a control catalyst (see below).

## 4.2 Transmetalation to **4c**

### 4.2.1 Influence of base and molecular sieves

*This experiment corresponds to the data shown in Figure 2A in the manuscript.*



In a culture tube, bismine triflate **4c** (17.7 mg, 0.025 mmol), phenylboronic acid (**1a**, 3.1 mg, 0.025 mmol),  $\text{Na}_3\text{PO}_4$  (8.2 mg, 0.05 mmol) and 20 mg of MS were mixed with anhydrous  $\text{CDCl}_3$  under an Ar atmosphere and the reaction was stirred for 3 h at  $60^\circ\text{C}$ . Then, 1,3,5-trimethoxybenzene was added as internal standard and the crude reactions were analyzed by  $^1\text{H}$  NMR to determine the yield of **6** (see Table S2).

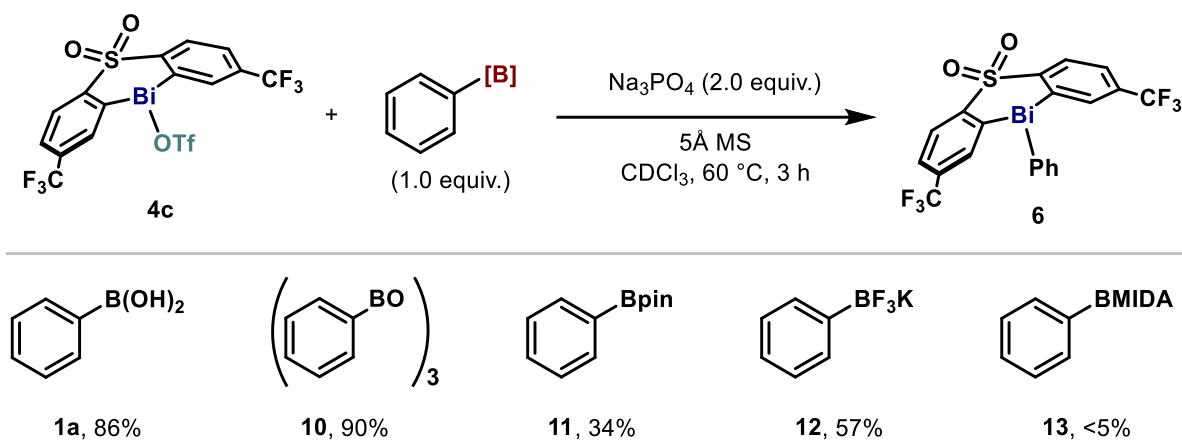
**Table S2.** Transmetalation to **4c** with phenylboronic acid **1a**. Yield calculated by  $^1\text{H}$  NMR using 1,3,5-trimethoxybenzene as internal standard.

entry	$[\text{MS}]$	$[\text{Na}_3\text{PO}_4]$	<b>6</b> , yield (%)	<b>3</b> , yield (%)
1	4Å MS	2.0 equiv.	82	14
2	4Å MS	-	65	21
3	5Å MS	2.0 equiv.	86	9
4	5Å MS	-	62	15
5	-	2.0 equiv.	21	73
6	-	-	traces	traces

#### 4.2.2 Use of other phenylboron compounds

In a culture tube, bismine triflate **4c** (17.7 mg, 0.025 mmol), phenylboronic acid derivative (0.025 mmol), Na<sub>3</sub>PO<sub>4</sub> (8.2 mg, 0.05 mmol) and 20 mg of 5Å MS were mixed with anhydrous CDCl<sub>3</sub> under an Ar atmosphere and the reaction was stirred for 3 h at 60 °C. Then, 1,3,5-trimethoxybenzene was added as internal standard and the crude reactions were analyzed by <sup>1</sup>H NMR to determine the yield of **6** (see Table S3).

**Table S3.** Transmetalation to **4c** with a variety of phenylboron compounds.

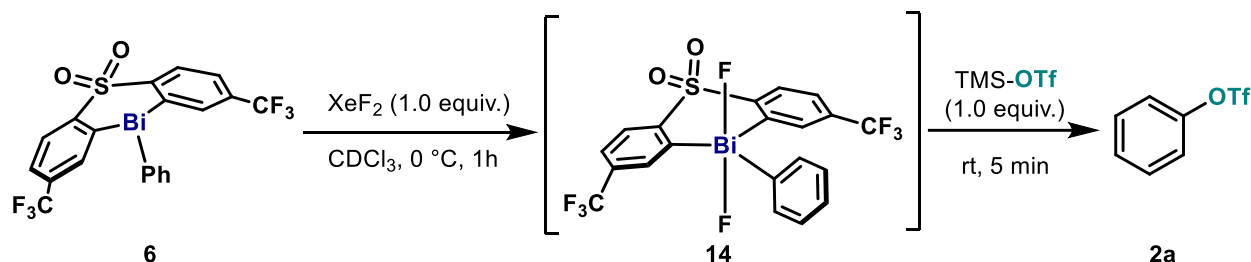


### 4.3 Oxidation with XeF<sub>2</sub> and reductive elimination in presence of TMSOTf

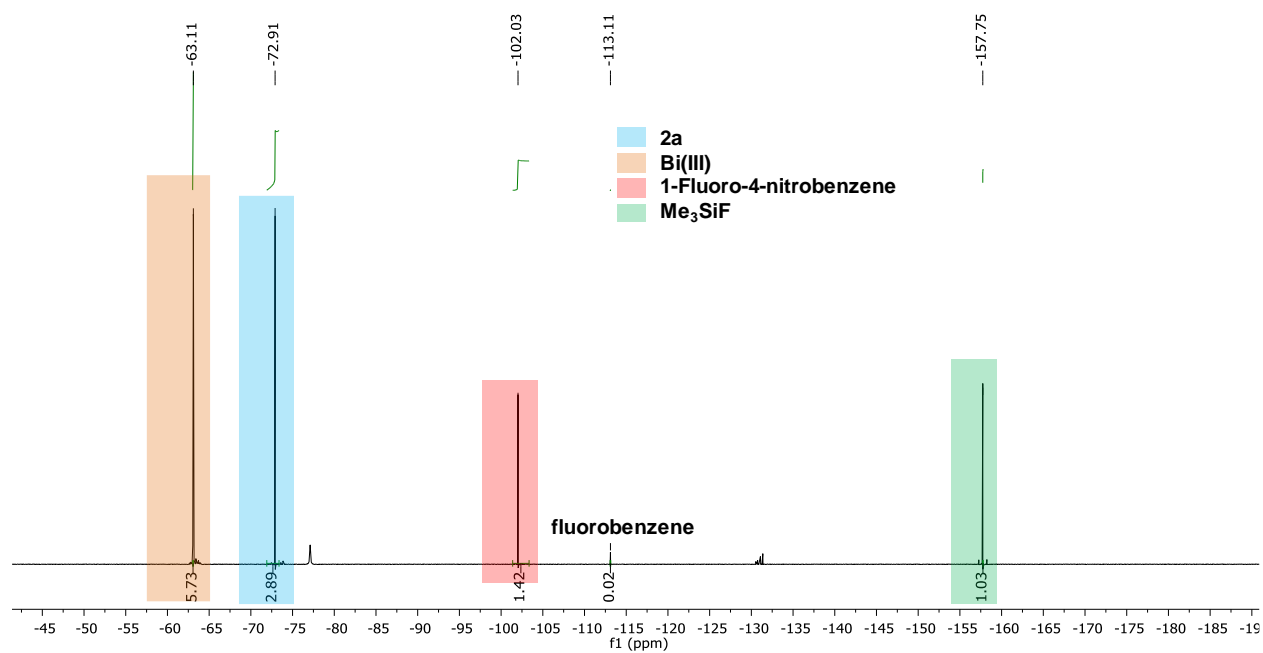
#### 4.3.1 One-pot oxidation-reductive elimination sequence

*This experiment corresponds to the data shown in Figure 2B in the manuscript.*

First, we performed a one-pot protocol consisting in a first oxidation with XeF<sub>2</sub> at 0 °C, followed by the addition of 1.0 equiv. of TMSOTf.



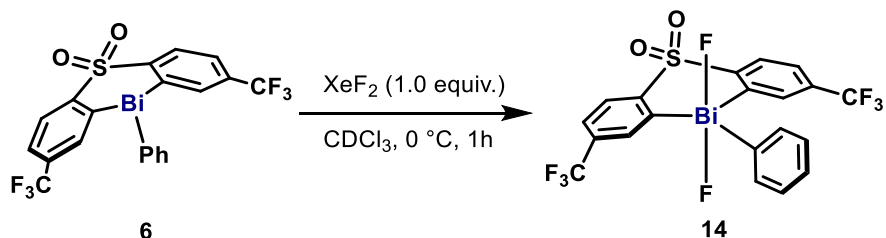
In a 10 mL Schlenk flask, phenyl bismine **6** (19.2 mg, 0.03 mmol) was mixed with anhydrous CDCl<sub>3</sub> (1 mL) under an Ar atmosphere and the reaction was cooled to 0 °C. Then, XeF<sub>2</sub> (5.1 mg, 0.03 mmol) were added at once as a solid, and the mixture was stirred for 1 h at 0 °C. Then, the reaction was warmed up to room temperature (ca. 22 °C) and TMSOTf was added with a micro syringe (5.4 μL, 0.03 mmol). After stirring for 5 min, 1-fluoro-4-nitrobenzene was added and the crude mixture was analyzed by <sup>19</sup>F NMR. Full conversion to **2a** was observed (>95%), together with the corresponding Me<sub>3</sub>SiF byproduct (see Figure S4).



**Figure S4.**  $^{19}\text{F}$  NMR analysis of the reaction crude after the one-pot oxidation-reductive elimination sequence using  $\text{XeF}_2$  (1.0 equiv.) and TMSOTf (1.0 equiv.) in  $\text{CDCl}_3$  at 90 °C.

#### 4.3.2 Synthesis and isolation of **14**

The synthesis and isolation of the Bi(V) difluoride species **14** was attempted following the protocol described below.



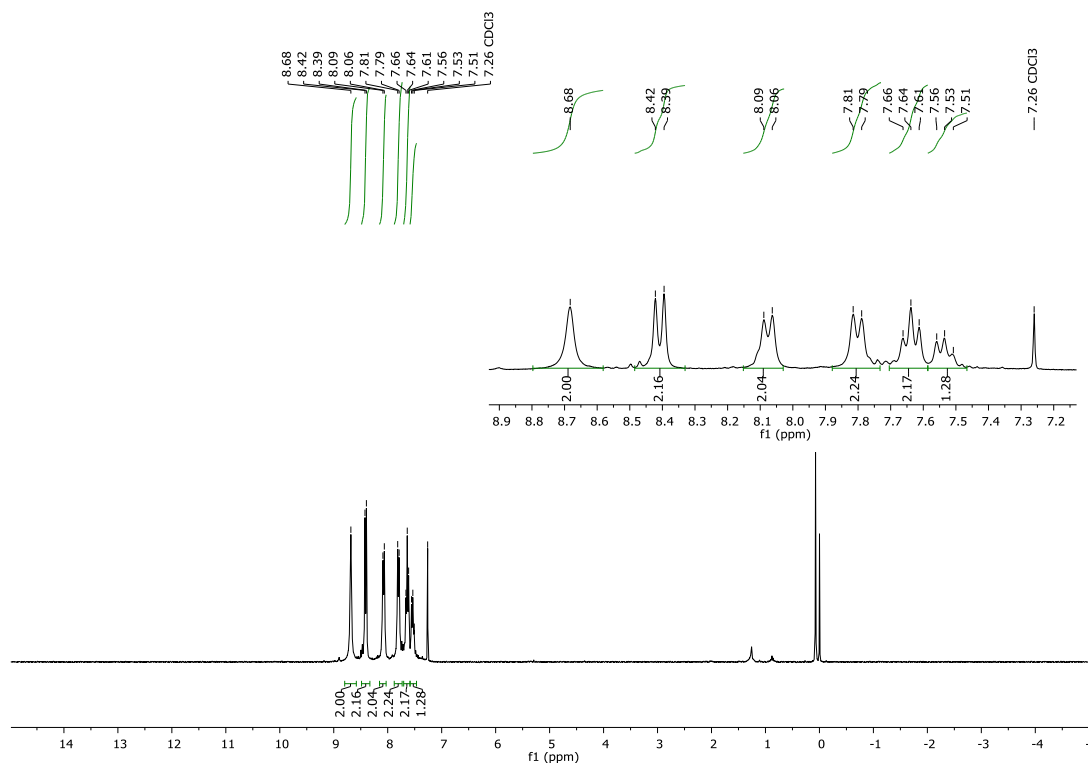
In a 10 mL Schlenk flask, phenyl bisimine **6** (128 mg, 0.2 mmol) was mixed with anhydrous  $\text{CHCl}_3$  (5 mL) under an Ar atmosphere and the reaction was cooled to  $0\text{ }^\circ\text{C}$ . Then,  $\text{XeF}_2$  (34 mg, 0.2 mmol) was added at once as a solid, and the mixture was stirred for 1 h at  $0\text{ }^\circ\text{C}$ . Then, pentane was added to the suspension (3 mL), and the solid was separated by decantation. The pale-yellow solid was washed with pentane ( $2 \times 2\text{ mL}$ ), and dried under vacuum for a period of 2 h. The title compound was obtained in >95% yield.

**$^1\text{H}$  NMR** - (500 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.68 (s, 2H), 8.40 (d,  $J = 8.1\text{ Hz}$ , 2H), 8.08 (d,  $J = 7.8\text{ Hz}$ , 2H), 7.80 (d,  $J = 8.0\text{ Hz}$ , 2H), 7.64 (t,  $J = 7.3\text{ Hz}$ , 2H), 7.53 (t,  $J = 7.3\text{ Hz}$ , 1H).

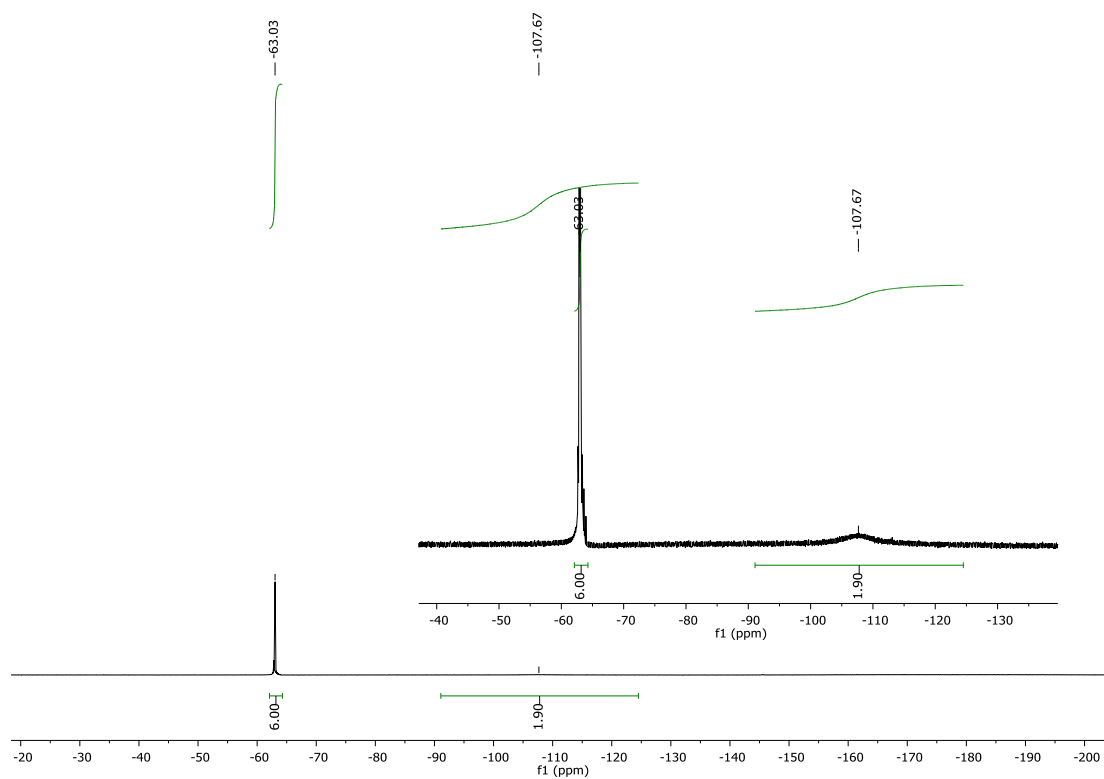
**$^{19}\text{F}$  NMR** - (471 MHz,  $\text{CDCl}_3$ ):  $\delta$  -63.0 (s, 6F), -107.7 (bs, 2F).

**HRMS (ESI,  $m/z$ ):** calc'd for  $\text{C}_{20}\text{H}_{11}\text{O}_2\text{S}_1\text{F}_9\text{Bi}^+$  [ $\text{M}+\text{F}$ ] $^-$  695.0135; found 695.0144.

Due to the low solubility of **14** and the appearance of broad bands,  $^{13}\text{C}$  NMR could not be obtained.



**Figure S5.** <sup>1</sup>H NMR of **14** in CDCl<sub>3</sub> at room temperature.

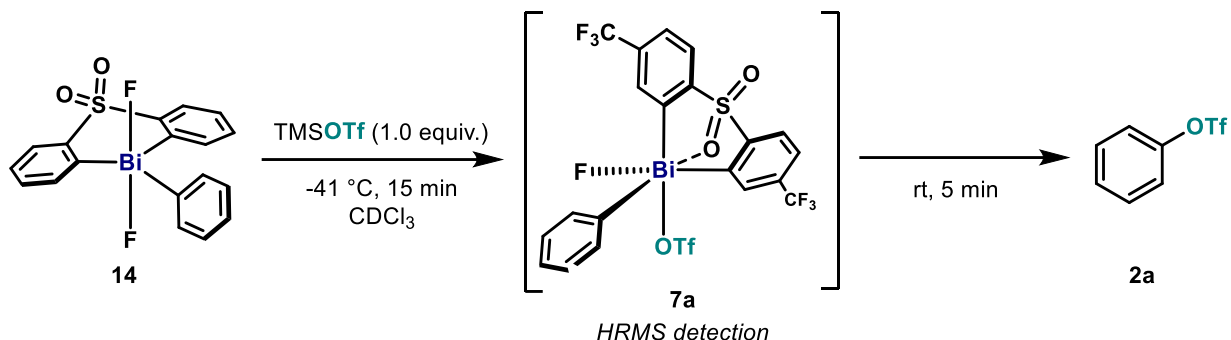


**Figure S6.** <sup>13</sup>C NMR of **14** in CDCl<sub>3</sub> at room temperature.

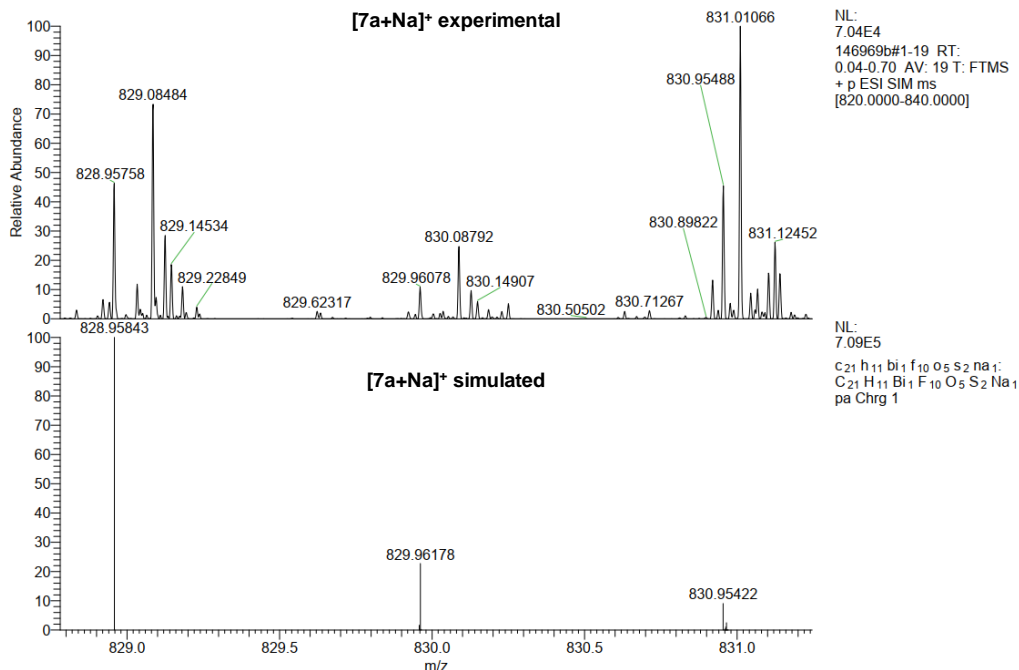


### 4.3.3 Reductive elimination from **7a** – HRMS studies

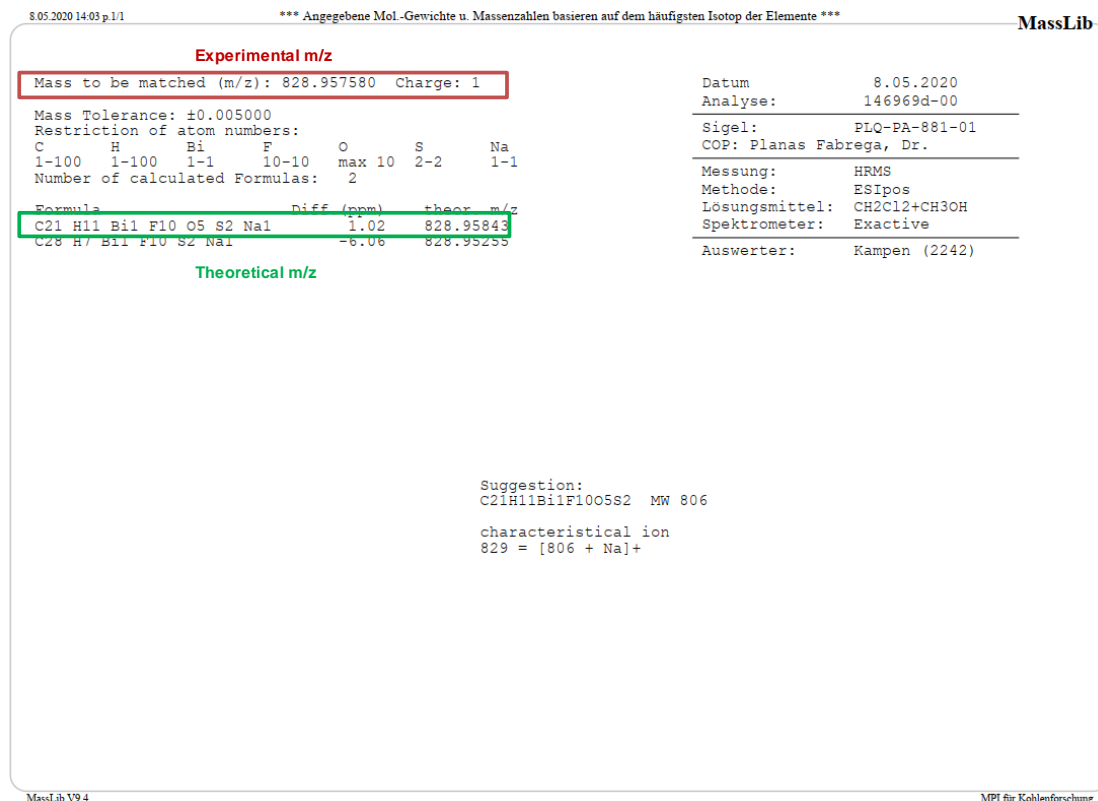
*This experiment corresponds to the data shown in Figure 2B in the manuscript.*



In a 10 mL Schlenk flask, difluoro bismine **14** (20.3 mg, 0.03 mmol) was mixed with anhydrous CDCl<sub>3</sub> (1 mL) under an Ar atmosphere and the reaction was cooled to -41 °C in a MeCN/N<sub>2</sub> cooling bath. Then TMSOTf (5.4 μL, 0.03 mmol) was added and the reaction was stirred for 15 min. Afterwards, an aliquot of the reaction was analyzed by HRMS (See Figure S7). **7a** was detected as a sodium adduct by ESI-HRMS analysis (C<sub>21</sub>H<sub>11</sub>F<sub>10</sub>O<sub>5</sub>S<sub>2</sub>BiNa<sup>+</sup>, *expt.* *m/z* = 828.9576; *calcd.* *m/z* = 828.9584; Figures S7 and S8). The crude reaction was warmed to room temperature (ca. 22 °C) and stirred for 5 min. Then, 1-fluoro-4-nitrobenzene was added and the crude mixture was analyzed by <sup>19</sup>F NMR. Full conversion to **2a** was observed (>95%), with traces of some byproducts.

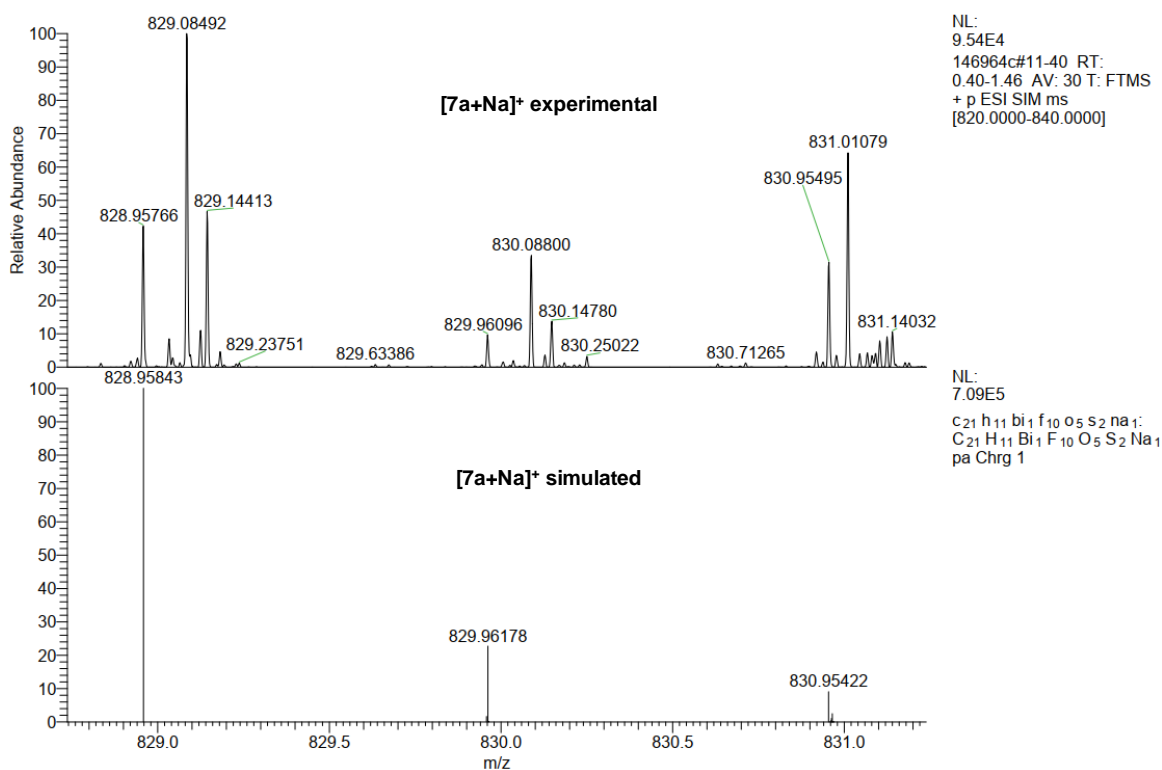


**Figure S7.** High-Resolution Mass Spectrum of the crude reaction of **14** and TMSOTf (top), showing a peak corresponding to  $[7a+Na]^+$ ; theoretical  $m/z$  of the peak corresponding to  $[7a+Na]^+$  (bottom).

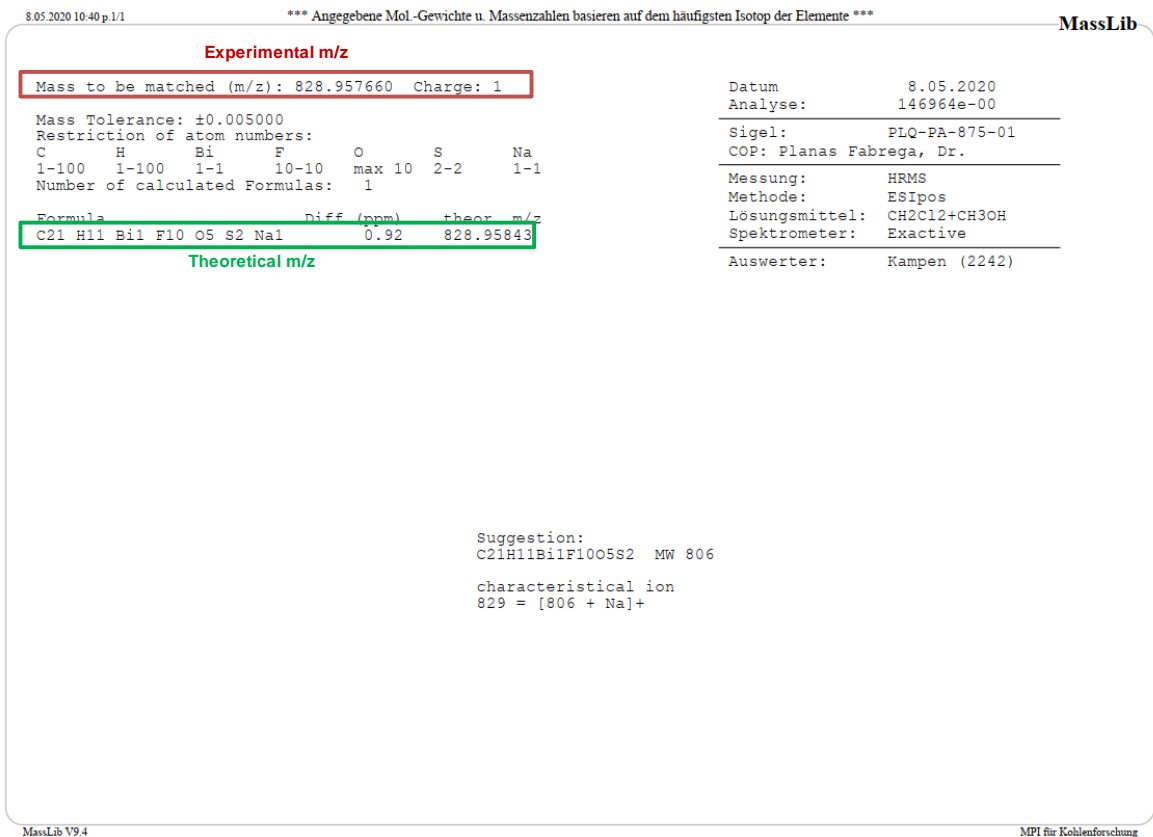


**Figure S8.** Detection of  $[7a+Na]^+$  by ESI-HRMS analysis of the reaction of **14** with TMSOTf.

When the reaction was performed with TIPSOTf (8.1  $\mu$ L, 0.03 mmol) instead of TMSOTf, **7a** was also detected as a sodium adduct by ESI-HRMS analysis ( $C_{21}H_{11}F_{10}O_5S_2BiNa^+$ , *expt.*  $m/z$  = 828.9577; *calcd.*  $m/z$  = 828.9584; Figures S9 and S10).



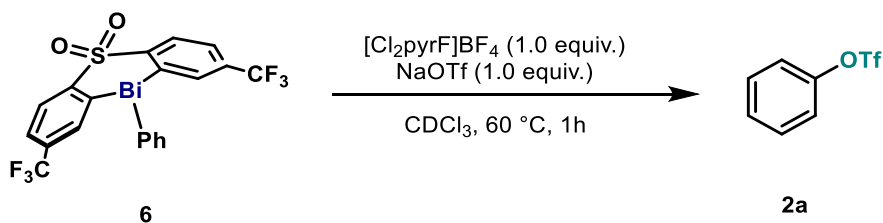
**Figure S9.** High-Resolution Mass Spectrum of the crude reaction of **14** and TIPSOTf (up), showing a peak corresponding to  $[7a+Na]^+$ ; theoretical  $m/z$  of the peak corresponding to  $[7a+Na]^+$  (bottom).



**Figure S10.** Detection of  $[7a+Na]^+$  by ESI-HRMS analysis of the reaction of **14** with TIPSOTf.

#### 4.4 Oxidation-reductive elimination sequence

*This experiment corresponds to the data shown in Figure 2B in the manuscript.*



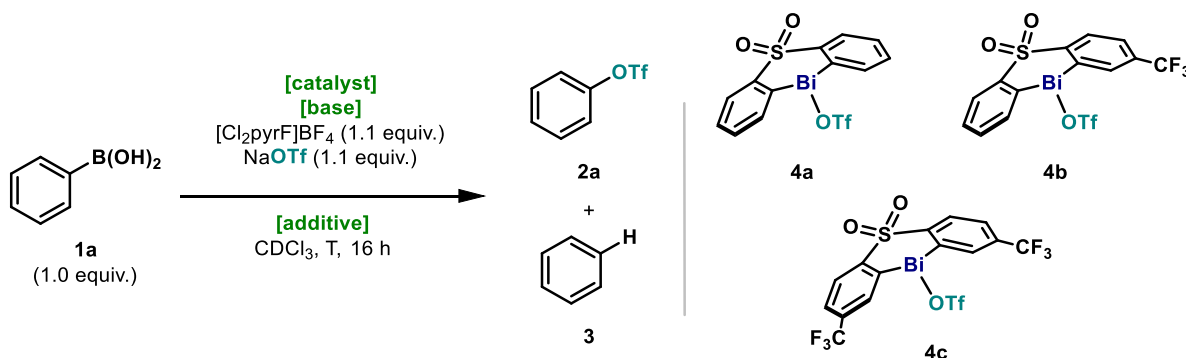
In a 10 mL Schlenk flask, phenyl bismine **6** (15.9 mg, 0.025 mmol), N-fluoro-2,6-dichloropyridinium tetrafluoroborate (6.3 mg, 0.025 mmol) and sodium triflate (4.3 mg, 0.025 mmol) were mixed with anhydrous CHCl<sub>3</sub> (1 mL) under an Ar atmosphere and the reaction was stirred at 60 °C for 1 h. Then, 1-fluoro-4-nitrobenzene was added and the crude mixture was analyzed by <sup>19</sup>F NMR, showing 92% yield of phenyl triflate **2a**.

When the reaction was performed with N-fluoro-2,6-dichloropyridinium trifluoromethanesulfonate ([Cl<sub>2</sub>pyrF]OTf) as oxidant, the yield of **2a** decreased substantially. The triflate salt is not fully soluble in CDCl<sub>3</sub> at 60 °C and after 1 h stirring at this temperature, it became a sticky insoluble solid.

## 5. Catalytic studies

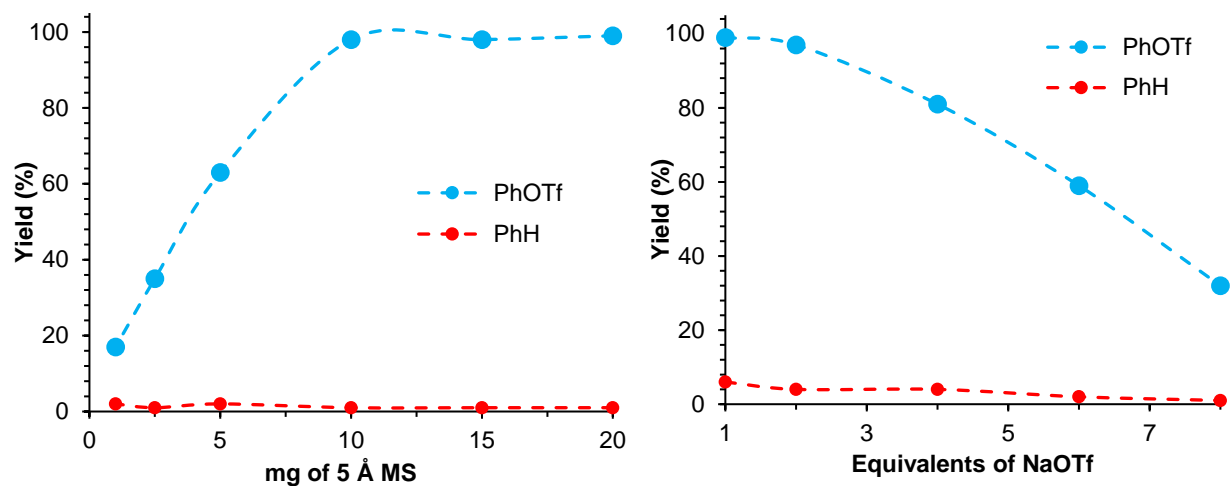
### 5.1 Optimization for the Bi-catalyzed coupling of arylboronic acids and NaOTf

General Procedure: A culture tube equipped with a stir bar was charged with phenylboronic acid (3.1 mg, 0.025 mmol). A teflon cap was fitted, and the tube was evacuated and refilled with Ar (3 cycles). The tube was transferred to a glove box, *bismine catalyst* (X mol%), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (7.0 mg, 1.1 equiv.), NaOTf (4.7 mg, 1.1 equiv.), *base* (Y equiv.) and additive (Z mg) were added. The tube was removed from the glove box and subjected to a positive pressure of Ar. CDCl<sub>3</sub> (0.5 mL) was added and the reaction was then stirred 16 h at the indicated temperature. Then, the yield was calculated by <sup>19</sup>F NMR using 1-fluoro-4-nitrobenzene as internal standard (addition by weight).

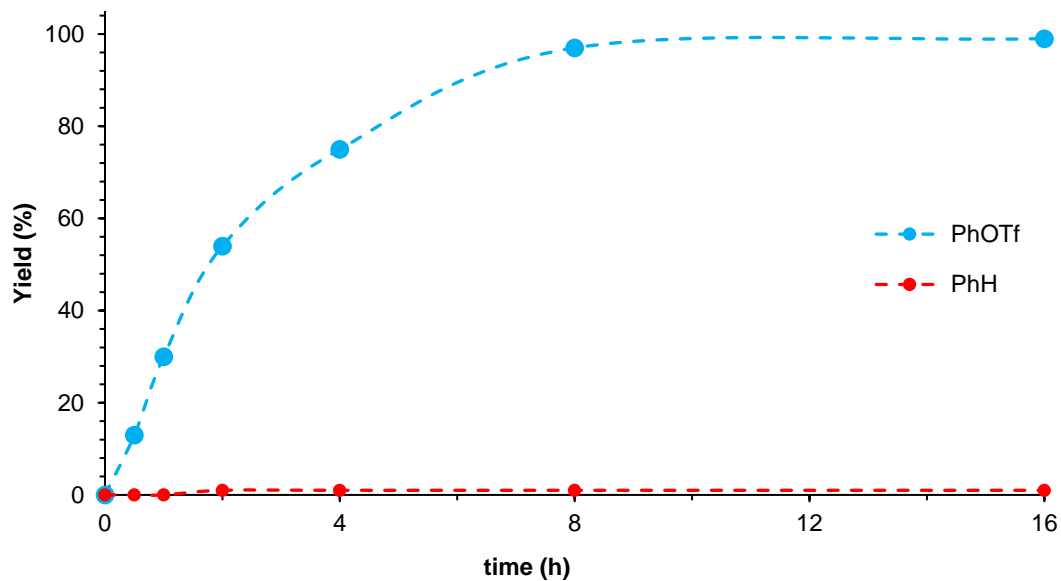
**Table S4.** Optimization of reaction conditions for the Bi-catalyzed formation of phenyl triflate**2a.** Yields calculated by  $^{19}\text{F}$  NMR using 1-fluoro-4-nitrobenzene as internal standard.

entry	base (Y equiv.)	catalyst (X mol%)	Additive (Z mg)	T ( $^{\circ}\text{C}$ )	2a, yield (%)	3, yield (%) <sup>a</sup>
1	$\text{K}_2\text{CO}_3$ (2)	<b>4c</b> (10)	-	60	31	5
2 <sup>b</sup>	$\text{K}_2\text{CO}_3$ (2)	<b>4c</b> (10)	-	60	4	<5
3	$\text{NaOAc}$ (2)	<b>4c</b> (10)	-	60	15	<5
4	$\text{NaO}^t\text{Bu}$ (2)	<b>4c</b> (10)	-	60	<5	<5
5	$\text{KOTMS}$ (2)	<b>4c</b> (10)	-	60	<5	<5
6	$\text{LiOMe}$ (2)	<b>4c</b> (10)	-	60	15	<5
7	$\text{CsF}$ (2)	<b>4c</b> (10)	-	60	<5	80
8	$\text{NaF}$ (2)	<b>4c</b> (10)	-	60	31	60
9	-	<b>4c</b> (10)	-	60	12	<5
10	$\text{K}_2\text{CO}_3$ (2)	<b>4a</b> (10)	-	60	6	<5
11	$\text{K}_2\text{CO}_3$ (2)	<b>4b</b> (10)	-	60	11	<5
12	$\text{K}_2\text{CO}_3$ (2)	<b>4c</b> (10)	4Å MS (20)	60	54	5
13	$\text{NaF}$ (2)	<b>4c</b> (10)	4Å MS (20)	60	84	15
14	$\text{Na}_2\text{CO}_3$ (2)	<b>4c</b> (10)	4Å MS (20)	60	64	<5
15	$\text{NaHCO}_3$ (2)	<b>4c</b> (10)	4Å MS (20)	60	86	13
16	$\text{Na}_3\text{PO}_4$ (2)	<b>4c</b> (10)	4Å MS (20)	60	93	6
17	-	<b>4c</b> (10)	4Å MS (20)	60	71	18
18	$\text{Na}_3\text{PO}_4$ (4)	<b>4c</b> (10)	4Å MS (20)	60	>95	<5
19	$\text{Na}_3\text{PO}_4$ (2)	<b>4c</b> (10)	5Å MS (10)	60	>95	<5
20	$\text{Na}_3\text{PO}_4$ (2)	<b>4c</b> (10)	5Å MS (5)	60	63	<5
21	$\text{Na}_3\text{PO}_4$ (2)	<b>4c</b> (5)	5Å MS (10)	60	21	<5
22	$\text{Na}_3\text{PO}_4$ (2)	<b>4c</b> (2.5)	5Å MS (10)	60	<5	<5
23	$\text{Na}_3\text{PO}_4$ (2)	<b>4c</b> (10)	5Å MS (10)	40	46	<5
24	$\text{Na}_3\text{PO}_4$ (2)	-	5Å MS (10)	60	<5	<5
25	$\text{Na}_3\text{PO}_4$ (2)	<b>BiPh<sub>3</sub></b> (10)	5Å MS (10)	60	<5	<5
26	$\text{Na}_3\text{PO}_4$ (2)	<b>BiCl<sub>3</sub></b> (10)	5Å MS (10)	60	<5	<5
27	$\text{Na}_3\text{PO}_4$ (2)	<b>L7</b> (10)	5Å MS (10)	60	<5	<5

<sup>a</sup>  $^1\text{H}$  NMR yield using 1-fluoro-4-nitrobenzene as internal standard; <sup>b</sup> Reaction run with PhBpin (**11**) instead of  $\text{PhB}(\text{OH})_2$  (**1a**).

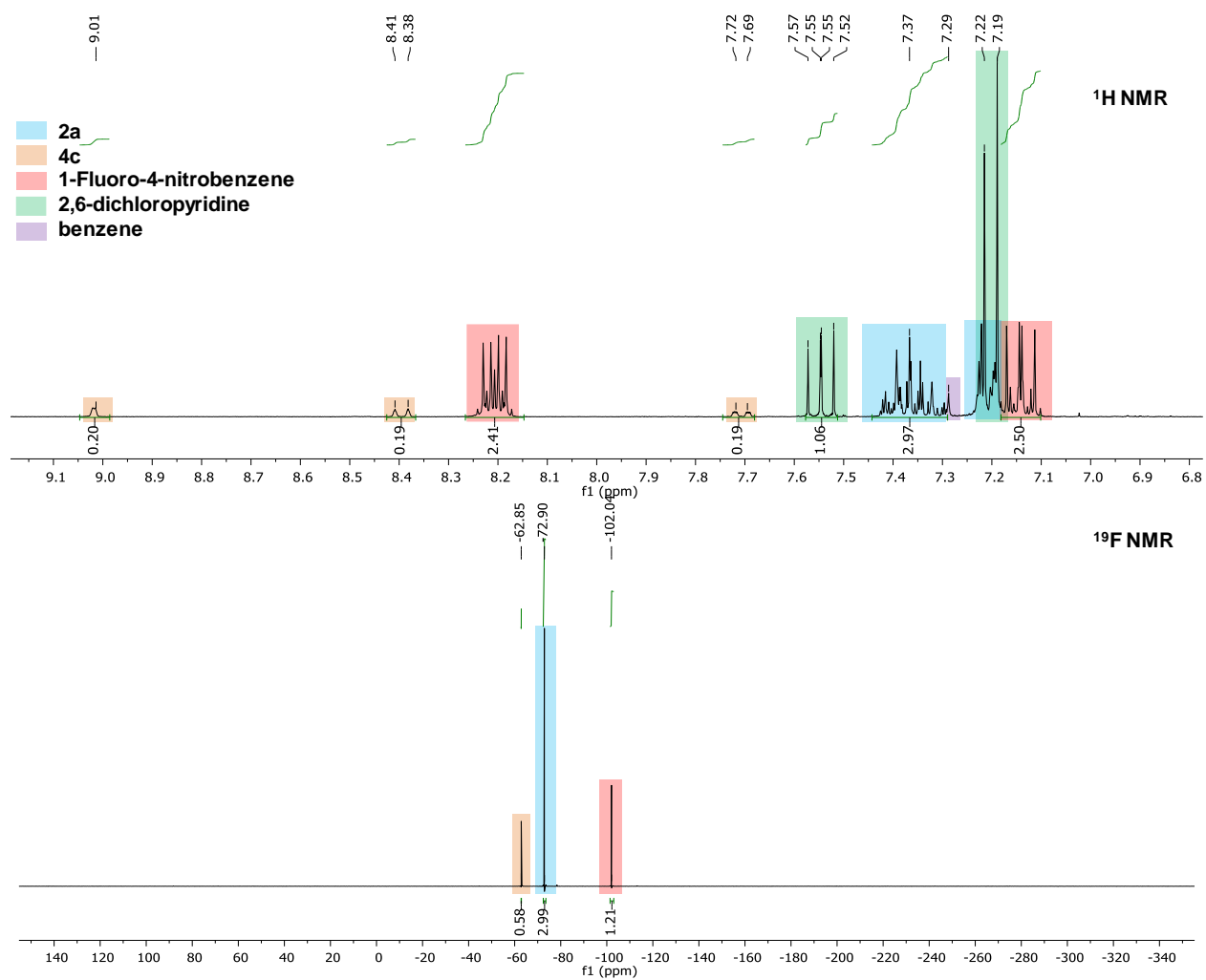


**Figure S11.** *Left:* Influence of the amount of 5 Å MS. Reaction run in presence of **1a** (0.025 mmol), [Cl<sub>2</sub>pyrF]BF<sub>4</sub> (0.03 mmol), NaOTf (0.03 mmol), Na<sub>3</sub>PO<sub>4</sub> (0.06 mmol), 5 Å MS (*x* mg) in CDCl<sub>3</sub> (0.5 mL) at 60 °C for 16 h. *Right:* Influence of the amount of NaOTf. Reaction run in presence of **1a** (0.025 mmol), [Cl<sub>2</sub>pyrF]BF<sub>4</sub> (0.03 mmol), NaOTf (*x* mmol), Na<sub>3</sub>PO<sub>4</sub> (0.06 mmol), 5 Å MS (10 mg) in CDCl<sub>3</sub> (0.5 mL) at 60 °C for 16 h.



**Figure S12.** Yield of **2a** at different time intervals. Reaction run in presence of **1a** (0.025 mmol), [Cl<sub>2</sub>pyrF]BF<sub>4</sub> (0.03 mmol), NaOTf (1.1 mmol), Na<sub>3</sub>PO<sub>4</sub> (0.06 mmol), 5 Å MS (10 mg) in CDCl<sub>3</sub> (0.5 mL) at 60 °C for *x* h.

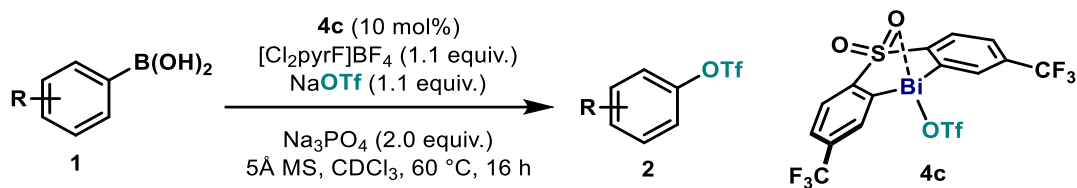




**Figure S13.**  $^1\text{H}$  NMR (top) and  $^{19}\text{F}$  NMR (bottom) analysis of the reaction crude after the Bi-catalyzed oxidative coupling of phenylboronic acid and sodium triflate with the reaction conditions described in Table S4, entry 19.

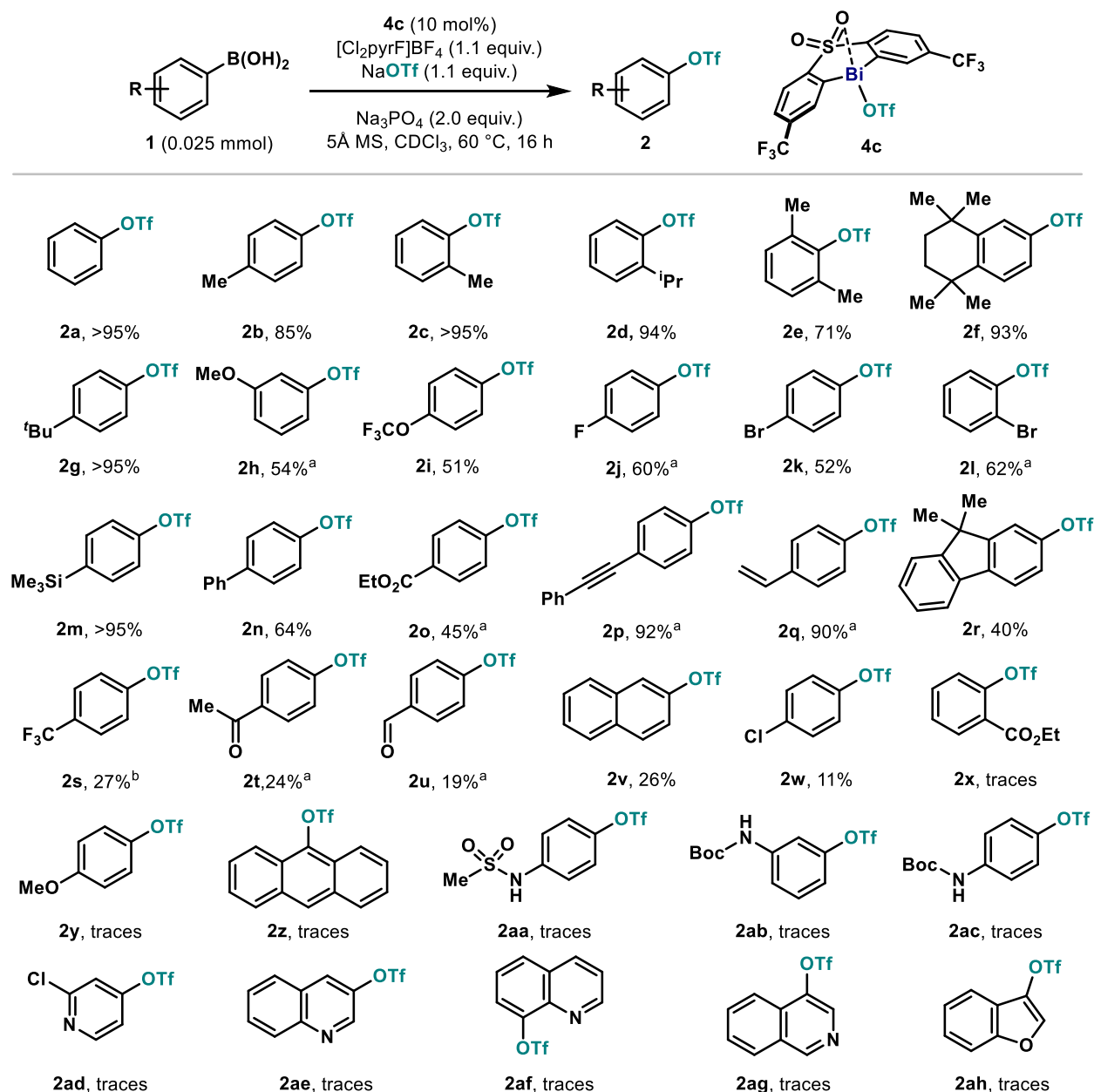
## 5.2 Scope of Bi-catalyzed coupling of arylboronic acids and NaOTf

### 5.2.1 General procedure for the NMR scale synthesis of aryl triflates



A culture tube equipped with a stirring bar was charged with aryl boronic acid (0.025 mmol, 1.0 equiv.), bismine **4c** (1.78 mg, 0.0025 mmol, 0.1 equiv.), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (6.98 mg, 0.0275 mmol, 1.1 equiv.), sodium triflate (4.73 mg, 0.0275 mmol, 1.1 equiv.), sodium phosphate (8.20 mg, 0.050 mmol, 2.0 equiv.), 5Å molecular sieves (10 mg) and dry CDCl<sub>3</sub> (1 mL) under an Ar atmosphere and stirred at 60 °C for 16 h. After this time, the yield was calculated by <sup>19</sup>F NMR using 1-fluoro-4-nitrobenzene (added by weight) as internal standard. Yield was determined by integration of the CF<sub>3</sub> group on the Ar–OTf moiety at a chemical shift ca. δ = 73.0 ppm.

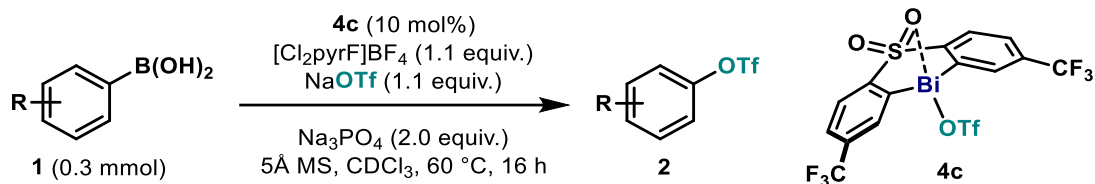
**Table S5.** Scope of the Bi-catalyzed coupling of arylboronic acids and NaOTf. Yields calculated by  $^{19}\text{F}$  NMR using 1-fluoro-4-nitrobenzene as internal standard



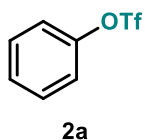
<sup>a</sup> Reaction run at 90 °C with 4 equiv. of  $\text{Na}_3\text{PO}_4$  and 20 mg of 5Å MS. <sup>b</sup> Reaction run with 2.0 equiv. NaF and 40 mg of 5Å MS.

Spectroscopic data for compounds **2a-r** was confirmed by isolation of the corresponding aryl triflates. Spectroscopic data for compounds **2s-w** was compared with previously reported characterization data.<sup>11-13</sup>

### 5.2.2 General procedure for synthesis of aryl triflates



A culture tube equipped with a stirring bar was charged with aryl boronic acid (0.30 mmol, 1.0 equiv.), bismine **4c** (21.3 mg, 0.03 mmol, 0.1 equiv.), 2,6-dichloro-1-fluoropyridinium tetrafluoroborate (83.8 mg, 0.33 mmol, 1.1 equiv.), sodium triflate (56.8 mg, 0.33 mmol, 1.1 equiv.), sodium phosphate (98.4 mg, 0.60 mmol, 2.0 equiv.), activated 5Å molecular sieves (120 mg) and dry  $\text{CHCl}_3$  (4 mL) under an Ar atmosphere and stirred at 60 °C for 16 h. After filtration, the crude material was purified by preparative TLC (hexanes/ $\text{CH}_2\text{Cl}_2$ ) to give the corresponding aryl triflate as colorless liquid or a white solid.



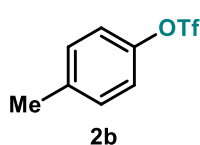
**Phenyl trifluoromethanesulfonate (2a):**<sup>13</sup> Following the general procedure, using 0.30 mmol of respective aryl boronic acid, **2a** was obtained in 90% yield as colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.49-7.34 (m, 3H), 7.31-7.24 (m, 2H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 149.8, 130.4, 128.6, 121.5, 118.9 (q, *J* = 320.1 Hz).

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -73.0 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>7</sub>H<sub>5</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 225.9906; found 225.9906.



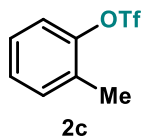
**p-Tolyl trifluoromethanesulfonate (2b):**<sup>14</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2b** was obtained in 81% yield as colorless liquid (Eluent: hexanes)

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.23-7.18 (m, 2H), 7.16-7.10 (m, 2H), 2.34 (s, 3H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 147.8, 138.7, 130.8, 121.1, 119.0 (q, *J* = 320.3 Hz), 20.9.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -73.1 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>8</sub>H<sub>7</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 240.0063; found 240.0065.



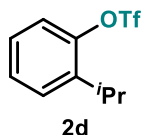
**o-Tolyl trifluoromethanesulfonate (2c):**<sup>13</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2c** was obtained in 93% yield as colorless liquid (Eluent: hexanes)

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.33-7.20 (m, 4H), 2.38 (s, 3H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 148.7, 132.3, 131.0, 128.4, 127.8 121.4, 118.8 (q, *J* = 320.1 Hz), 16.4.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -74.0 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>8</sub>H<sub>7</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 240.0063; found 240.0066.



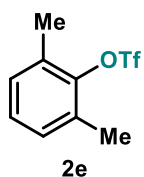
**2-Isopropylphenyl trifluoromethanesulfonate (2d):**<sup>11</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2d** was obtained in 87% yield as colorless liquid (Eluent: hexanes)

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.43-7.21 (m, 4H), 3.30 (m, *J* = 6.9 Hz, 1H), 1.27 (d, *J* = 6.9 Hz, 6H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 147.3, 141.4, 128.7, 128.0, 127.6, 121.3, 118.5 (q, *J* = 320.2 Hz), 27.3, 23.3.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -74.0 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>10</sub>H<sub>11</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 268.0376; found 268.0376.



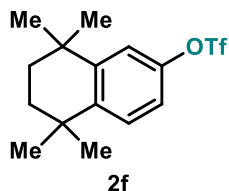
**2,6-Dimethylphenyl trifluoromethanesulfonate (2e):**<sup>11</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2e** was obtained in 70% yield as colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.18-7.07 (m, 3H), 2.40 (s, 6H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 147.1, 131.7, 130.0, 128.1, 118.8 (q, *J* = 319.9 Hz), 17.2.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -73.6 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>9</sub>H<sub>9</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 254.0219; found 254.0219.



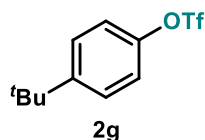
**5,5,8,8-Tetramethyl-5,6,7,8-tetrahydronaphthalen-2-yl trifluoromethanesulfonate (2f):** Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2f** was obtained in 85% yield as colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.35 (d, *J* = 8.8 Hz, 1H), 7.15 (d, *J* = 2.7 Hz, 1H), 7.01 (dd, *J* = 8.8, 2.7 Hz, 1H), 1.70 (s, 4H), 1.28 (s, 12H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 147.9, 147.8, 145.5, 128.6, 119.1, 119.0 (q, *J* = 320.4 Hz), 118.4, 34.9, 34.9, 34.8, 34.4, 31.9, 31.8.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -73.0 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>15</sub>H<sub>19</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 336.1002; found 336.1002.



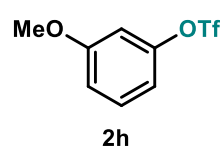
**4-(*Tert*-butyl)phenyl trifluoromethanesulfonate (2g):**<sup>15</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2g** was obtained in 93% yield as colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.48-7.42 (m, 2H), 7.22-7.16 (m, 2H), 1.33 (s, 9H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 151.8, 147.6, 127.3, 120.8, 118.9 (q, *J* = 320.6 Hz), 34.9, 31.4.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -73.0 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>11</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 282.0532; found 282.0532.



**3-Methoxyphenyl trifluoromethanesulfonate (2h):**<sup>16</sup> Following the general procedure at 90 °C and using 4.0 equivalents of Na<sub>3</sub>PO<sub>4</sub>, 240 mg of dry 5Å molecular sieves and 0.3 mmol of respective aryl boronic acid, **2h** was obtained

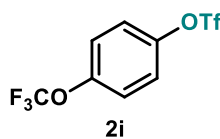
in 51% yield as colorless liquid (Eluent: hexanes/CH<sub>2</sub>Cl<sub>2</sub> 4:1).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.34 (t, *J* = 8.4 Hz, 1H), 6.93 (ddd, *J* = 8.4, 2.4, 0.9 Hz, 1H), 6.87 (ddd, *J* = 8.4, 2.4, 0.9 Hz, 1H), 6.81 (t, *J* = 2.4 Hz, 1H), 3.83 (s, 3H) .

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 161.0, 150.4, 130.7, 118.9 (q, *J* = 320.0 Hz), 114.3, 113.4, 107.6, 55.8.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -72.9 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>8</sub>H<sub>7</sub>F<sub>3</sub>O<sub>4</sub>S [M]<sup>+</sup> 256.0012; found 256.0013.



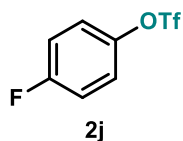
**4-(Trifluoromethoxy)phenyl trifluoromethanesulfonate (2i):**<sup>17</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2i** was obtained in 50% yield as colorless liquid (Eluent: hexanes/CH<sub>2</sub>Cl<sub>2</sub> 4:1).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.36-7.28 (m, 4H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 148.7 (q, *J* = 2.0 Hz), 147.5, 123.1, 122.9, 120.5 (q, *J* = 258.4 Hz), 118.9 (q, *J* = 320.6 Hz).

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -58.3(s, 3F), -72.8 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>8</sub>H<sub>4</sub>F<sub>6</sub>O<sub>4</sub>S [M]<sup>+</sup> 309.9729; found 309.9730.



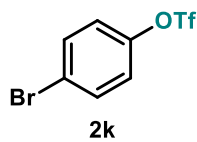
**4-Fluorophenyl trifluoromethanesulfonate (2j):**<sup>15</sup> Following the general procedure at 90 °C and using 4.0 equivalents of Na<sub>3</sub>PO<sub>4</sub>, 240 mg of dry 5Å molecular sieves and 0.3 mmol of respective aryl boronic acid, **2j** was obtained in 60% yield as colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.31-7.23 (m, 2H), 7.19-7.09 (m, 2H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 161.8 (q, *J* = 248.8 Hz), 145.4 3 (q, *J* = 3.93 Hz), 123.3 (d, *J* = 8.9 Hz), 118.9 (d, *J* = 320.7 Hz), 117.3 (d, *J* = 24.3 Hz).

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -72.8 (s, 3F), -112.4 (s, 1F).

**HRMS (EI, m/z):** calc'd for C<sub>7</sub>H<sub>4</sub>F<sub>4</sub>O<sub>3</sub>S [M]<sup>+</sup> 243.9812; found 243.9814.



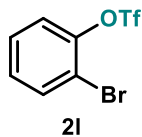
**4-Bromophenyl trifluoromethanesulfonate (2k):**<sup>18</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2k** was obtained in 49% yield as colorless liquid (Eluent: hexanes/CH<sub>2</sub>Cl<sub>2</sub> 4:1).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.62-7.55 (m, 2H), 7.20-7.13 (m, 2H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 148.6, 133.6, 125.2, 122.2, 118.8 (q, *J* = 320.5 Hz).

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -72.7 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>7</sub>H<sub>4</sub>BrF<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 303.9011; found 303.9013.



**2-Bromophenyl trifluoromethanesulfonate (2l):**<sup>19</sup> Following the general procedure at 90 °C and using 4.0 equivalents of Na<sub>3</sub>PO<sub>4</sub>, 240 mg of dry 5Å molecular sieves and 0.3 mmol of respective aryl boronic acid, **2l** was obtained in 61% yield as colorless liquid (Eluent: hexanes/CH<sub>2</sub>Cl<sub>2</sub> 4:1).

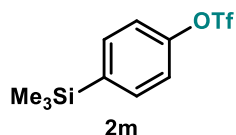
**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.72-7.66 (m, 1H), 7.43-7.33 (m, 2H), 7.30-7.22 (m, 1H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 147.2, 134.6, 129.6, 129.2, 123.1, 118.8 (q, *J* = 320.2 Hz), 116.2.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -73.4 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>7</sub>H<sub>4</sub>BrF<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 303.9011; found 303.9013.





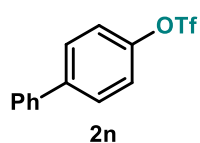
**4-(Trimethylsilyl)phenyl trifluoromethanesulfonate (2m):**<sup>20</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2m** was obtained in 96% yield as colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.62-7.55 (m, 2H), 7.28-7.21 (m, 2H), 0.28 (s, 9H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 150.4, 141.8, 135.4, 120.6, 118.9 (q, *J* = 320.6 Hz), -1.1.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -73.0 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>10</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>SSi [M]<sup>+</sup> 298.0301; found 298.0298.



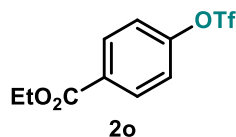
**[1,1'-Biphenyl]-4-yl trifluoromethanesulfonate (2n):**<sup>21</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2n** was obtained in 63% yield as a white solid (Eluent: hexanes/CH<sub>2</sub>Cl<sub>2</sub> 4:1).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.69-7.62 (m, 2H), 7.60-7.54 (m, 2H), 7.52-7.39 (m, 3H), 7.39-7.33 (m, 2H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 149.1, 141.8, 139.4, 129.1, 129.0, 128.2, 127.3, 121.8, 119.0 (q, *J* = 320.5 Hz).

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -72.8 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>13</sub>H<sub>9</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 302.0219; found 302.0222.



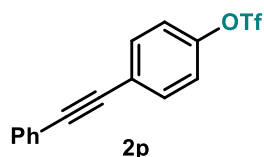
**Ethyl 4-(((trifluoromethyl)sulfonyl)oxy)benzoate (2o):**<sup>13</sup> Following the general procedure at 90 °C and using 4.0 equivalents of Na<sub>3</sub>PO<sub>4</sub>, 240 mg of dry 5 Å molecular sieves and 0.3 mmol of respective aryl boronic acid, **2o** was obtained in 42% yield as colorless liquid (Eluent: hexanes/CH<sub>2</sub>Cl<sub>2</sub> 3:1).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 8.18-8.11 (m, 2H), 7.38-7.31 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 165.1, 152.6, 132.0, 130.9, 121.5, 118.9 (q, *J* = 320.7 Hz), 61.7, 14.4.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -72.8 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>10</sub>H<sub>9</sub>F<sub>3</sub>O<sub>5</sub>S [M]<sup>+</sup> 298.0117; found 298.0116.



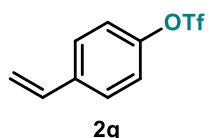
**4-(Phenylethynyl)phenyl trifluoromethanesulfonate (2p):**<sup>22</sup> Following the general procedure at 90 °C and using 4.0 equivalents of Na<sub>3</sub>PO<sub>4</sub>, 240 mg of dry 5 Å molecular sieves and 0.3 mmol of respective aryl boronic acid, **2p** was obtained in 86% yield as white solid (Eluent: hexanes/CH<sub>2</sub>Cl<sub>2</sub> 3:1).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.63-7.56 (m, 2H), 7.56-7.48 (m, 2H), 7.40-7.32 (m, 3H), 7.29-7.21 (m, 2H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 149.1, 133.5, 131.8, 128.9, 128.6, 124.2, 122.7, 121.6, 118.9 (q, *J* = 320.8 Hz), 91.4, 87.5.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -72.8 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>15</sub>H<sub>9</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 326.0219; found 326.0225.



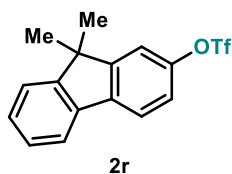
**4-Vinylphenyl trifluoromethanesulfonate (2q):**<sup>23</sup> Following the general procedure at 90 °C and using 4.0 equivalents of Na<sub>3</sub>PO<sub>4</sub>, 240 mg of dry 5 Å molecular sieves and 0.3 mmol of respective aryl boronic acid, **2q** was obtained in 78% yield as colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.50-7.41 (m, 2H), 7.27-7.18 (m, 2H), 6.70 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.76 (dd, *J* = 17.6, 0.7 Hz, 1H), 5.34 (dd, *J* = 10.8, 0.7 Hz, 1H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 149.0, 138.1, 135.2, 128.0, 121.6, 118.7 (q, *J* = 320.5 Hz), 116.1.

**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -72.9 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>9</sub>H<sub>7</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 252.0063; found 252.0064.



**9,9-Dimethyl-9H-fluoren-2-yl trifluoromethanesulfonate (2r):** Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **2r** was obtained in 38% yields as colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (300 MHz, CDCl<sub>3</sub>): δ 7.76-7.66 (m, 2H), 7.47-7.40 (m, 1H), 7.39-7.32 (m, 2H), 7.32-7.28 (m, 1H), 7.26-7.19 (m, 1H), 1.49 (s, 6H).

**<sup>13</sup>C NMR** - (75 MHz, CDCl<sub>3</sub>): δ 156.1, 153.9, 149.0, 139.6, 137.5, 128.2, 127.5, 122.9, 121.2, 120.5, 120.3, 119.0 (q, *J* = 320.9 Hz), 116.2, 47.5, 27.0.

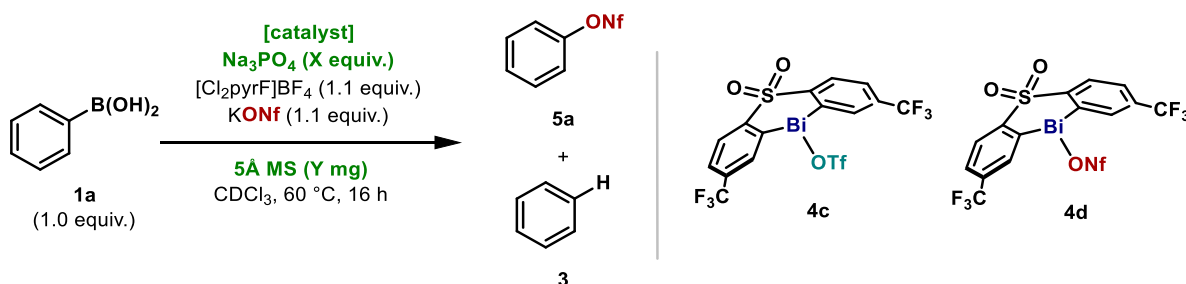
**<sup>19</sup>F NMR** - (282 MHz, CDCl<sub>3</sub>): δ -72.8 (s, 3F).

**HRMS (EI, m/z):** calc'd for C<sub>16</sub>H<sub>13</sub>F<sub>3</sub>O<sub>3</sub>S [M]<sup>+</sup> 342.0532; found 342.0531.

### 5.3 Optimization for the Bi-catalyzed coupling of arylboronic acids and KONf

**General Procedure:** A culture tube equipped with a stir bar was charged with phenylboronic acid (3.1 mg, 0.025 mmol). A teflon cap was fitted, and the tube was evacuated and refilled with Ar (3 cycles). The tube was transferred to a glove box, *bismine catalyst* (X mol%), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (7.0 mg, 1.1 equiv.), KONf (9.3 mg, 1.1 equiv.), Na<sub>3</sub>PO<sub>4</sub> (Y equiv.) and 5 Å molecular sieves (Z mg) were added. The tube was removed from the glove box and subjected to a positive pressure of Ar. CDCl<sub>3</sub> (0.5 mL) was added and the reaction was then stirred 16 h at the corresponding temperature. After the indicated time, the yield was calculated by <sup>19</sup>F NMR using 1-fluoro-4-nitrobenzene as internal standard (addition by weight).

**Table S6.** Optimization of reaction conditions for the Bi-catalyzed formation of phenyl nonaflate **5a**. Yields calculated by <sup>19</sup>F NMR using 1-fluoro-4-nitrobenzene as internal standard.



entry	Na <sub>3</sub> PO <sub>4</sub> (Y equiv.)	catalyst (X mol%)	5 Å MS (Z mg)	5a, yield (%)	3, yield (%) <sup>a</sup>
1 <sup>b</sup>	2	4c (10)	10	56	<5
2	2	4d (5)	10	36	<5
3	2	4d (10)	10	83	<5
4	2	4d (15)	10	>95	<5
5 <sup>c</sup>	2	4d (10)	10	86	<5
6 <sup>d</sup>	2	4d (10)	10	82	<5
7	4	4d (10)	20	>95	<5

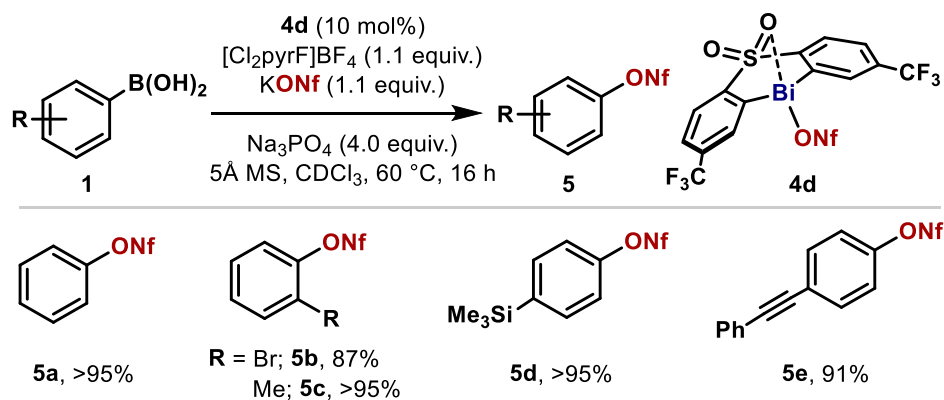
<sup>a</sup> <sup>1</sup>H NMR yield using 1-fluoro-4-nitrobenzene as internal standard; <sup>b</sup> Phenyltriflate **2a** was also detected in 9% yield. <sup>c</sup> Reaction run for 24 h. <sup>d</sup> Reaction run at 80 °C.

## 5.4 Scope of Bi-catalyzed coupling of arylboronic acids and KONf

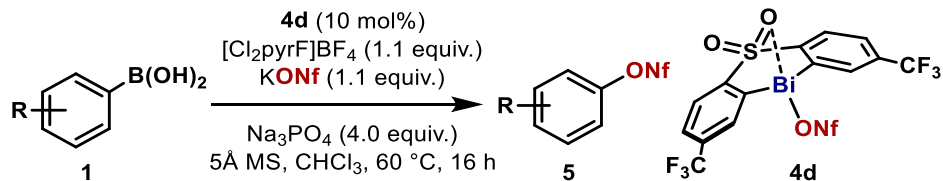
### 5.4.1 General procedure for the NMR scale synthesis of aryl nonaflates

A culture tube equipped with a stir bar was charged with aryl boronic acid (0.025 mmol, 1.0 equiv.), bismine **4d** (2.15 mg, 0.0025 mmol, 0.1 equiv.), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (6.98 mg, 0.0275 mmol, 1.1 equiv.), potassium nonaflate (9.30 mg, 0.0275 mmol, 1.1 equiv.), sodium phosphate (16.39 mg, 0.10 mmol, 4.0 equiv.), 5 Å molecular sieves (20 mg) and dry CDCl<sub>3</sub> (1 mL) under an Ar atmosphere and stirred at 60 °C for 16 h. After the indicated time, the yield was calculated by <sup>19</sup>F NMR using 1-fluoro-4-nitrobenzene as internal standard. Yield was determined by integration of the –CF<sub>2</sub>– group on the Ar–ONf moiety at a chemical shift ca. δ = -109.0 ppm.

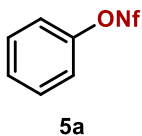
**Table S7.** Scope of the Bi-catalyzed coupling of arylboronic acids and NaOTf. Yields calculated by <sup>19</sup>F NMR using 1-fluoro-4-nitrobenzene as internal standard.



#### 5.4.2 General procedure for synthesis of aryl nonaflates



A culture tube equipped with a stir bar was charged with aryl boronic acid (0.30 mmol, 1.0 equiv.), bismine **4d** (25.8 mg, 0.03 mmol, 0.1 equiv.), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (83.8 mg, 0.33 mmol, 1.1 equiv.), potassium nonaflate (111.6 mg, 0.33 mmol, 1.1 equiv.), sodium phosphate (196.8 mg, 1.20 mmol, 4.0 equiv.), 5Å molecular sieves (240 mg) and dry  $\text{CHCl}_3$  (4 mL) under an Ar atmosphere and stirred vigorously at 60 °C for 16 h. After filtration, the crude material was purified by preparative TLC (hexanes/ $\text{CH}_2\text{Cl}_2$ ) to give the corresponding aryl nonaflate as colourless liquid or a white solid.



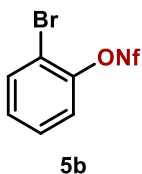
**Phenyl nonafluorobutane-1-sulfonate (5a):**<sup>24</sup> Following the general procedure, using 0.30 mmol of respective aryl boronic acid, **5a** was obtained in 97% yield as colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (500 MHz, CDCl<sub>3</sub>): δ 7.49-7.43 (m, 2H), 7.42-7.37 (m, 1H), 7.32-7.27 (m, 2H).

**<sup>13</sup>C {<sup>19</sup>F} NMR** - (126 MHz, CDCl<sub>3</sub>): δ 150.0, 130.4, 128.5, 121.5, 117.2, 114.9, 110.0, 108.6.

**<sup>19</sup>F NMR** - (471 MHz, CDCl<sub>3</sub>): δ -80.7– -80.8 (m, 3F), -109.0– -109.1 (m, 2F), -120.8– -121.0 (m, 2F), -125.8– -126.0 (m, 2F).

**HRMS (EI, m/z):** calc'd for C<sub>10</sub>H<sub>5</sub>F<sub>9</sub>O<sub>3</sub>S [M]<sup>+</sup> 375.9810; found 375.9817.



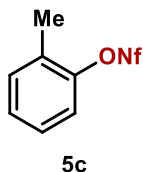
**2-Bromophenyl nonafluorobutane-1-sulfonate (5b):**<sup>25</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **5b** was obtained in 82% yield as colorless liquid (Eluent: hexanes/CH<sub>2</sub>Cl<sub>2</sub> 5:1).

**<sup>1</sup>H NMR** - (500 MHz, CDCl<sub>3</sub>): δ 7.69 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.43-7.34 (m, 2H), 7.28-7.23 (m, 1H).

**<sup>13</sup>C {<sup>19</sup>F} NMR** - (126 MHz, CDCl<sub>3</sub>): δ 147.4, 134.7, 129.6, 129.2, 123.1, 117.2, 116.4, 114.8, 110.0, 108.6.

**<sup>19</sup>F NMR** - (471 MHz, CDCl<sub>3</sub>): δ -80.6– -80.7 (m, 3F), -109.1– -109.3 (m, 2F), -120.6– -120.8 (m, 2F), -125.7– -125.9 (m, 2F).

**HRMS (EI, m/z):** calc'd for C<sub>10</sub>H<sub>4</sub>BrF<sub>9</sub>O<sub>3</sub>S [M]<sup>+</sup> 453.8915; found 453.8918.



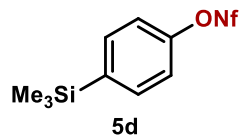
**o-Tolyl nonafluorobutane-1-sulfonate (5c):**<sup>25</sup> Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **5c** was obtained in 93% yield as colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (500 MHz, CDCl<sub>3</sub>): δ 7.32-7.23 (m, 4H), 2.39 (s, 3H).

**<sup>13</sup>C {<sup>19</sup>F} NMR** - (126 MHz, CDCl<sub>3</sub>): 148.9, 132.4, 131.2, 128.4, 127.8, 121.5, 117.3, 114.6, 110.1, 108.7, 16.6.

**<sup>19</sup>F NMR** - (471 MHz, CDCl<sub>3</sub>): δ -80.7– -80.8 (m, 3F), -109.8– -110.0 (m, 2F), -120.8– -120.9 (m, 2F), -125.8– -125.9 (m, 2F).

**HRMS (EI, m/z):** calc'd for C<sub>11</sub>H<sub>7</sub>F<sub>9</sub>O<sub>3</sub>S [M]<sup>+</sup> 389.9967; found 389.9974.



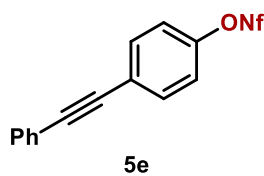
**4-(Trimethylsilyl)phenyl nonafluorobutane-1-sulfonate (5d):** Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **5d** was obtained in 96% yield as a colorless liquid (Eluent: hexanes).

**<sup>1</sup>H NMR** - (500 MHz, CDCl<sub>3</sub>): δ 7.60-7.56 (m, 2H), 7.27-7.23 (m, 2H), 0.28 (s, 9H).

**<sup>13</sup>C {<sup>19</sup>F} NMR** - (126 MHz, CDCl<sub>3</sub>): 150.7, 141.8, 135.4, 120.7, 117.2, 114.9, 110.0, 108.6, -1.1.

**<sup>19</sup>F NMR** - (471 MHz, CDCl<sub>3</sub>): δ -80.7– -80.8 (m, 3F), -109.0– -109.1 (m, 2F), -120.8– -121.0 (m, 2F), -125.8– -126.0 (m, 2F).

**HRMS (ESI, m/z):** calc'd for C<sub>13</sub>H<sub>13</sub>F<sub>9</sub>O<sub>3</sub>SSi [M]<sup>+</sup> 448.0206; found 448.0206.



**4-(Phenylethynyl)phenyl nonafluorobutane-1-sulfonate (5e):** Following the general procedure, using 0.3 mmol of respective aryl boronic acid, **5e** was obtained in 92% yield as a white solid (Eluent: hexanes/CH<sub>2</sub>Cl<sub>2</sub> 3:1).

**<sup>1</sup>H NMR** - (500 MHz, CDCl<sub>3</sub>): δ 7.63-7.58 (m, 2H), 7.57-7.52 (m, 2H), 7.40-7.35 (m, 3H), 7.30-7.26 (m, 2H).

**<sup>13</sup>C {<sup>19</sup>F} NMR** - (126 MHz, CDCl<sub>3</sub>): 149.3, 133.5, 131.8, 128.9, 128.6, 124.1, 122.7, 121.7, 117.2, 115.0, 110.0, 108.6, 91.4, 87.5.

**<sup>19</sup>F NMR** - (471 MHz, CDCl<sub>3</sub>): δ -80.6– -80.7 (m, 3F), -108.7– -108.9 (m, 2F), -120.6 – -121.0 (m, 2F), -125.7- -125.9 (m, 2F).

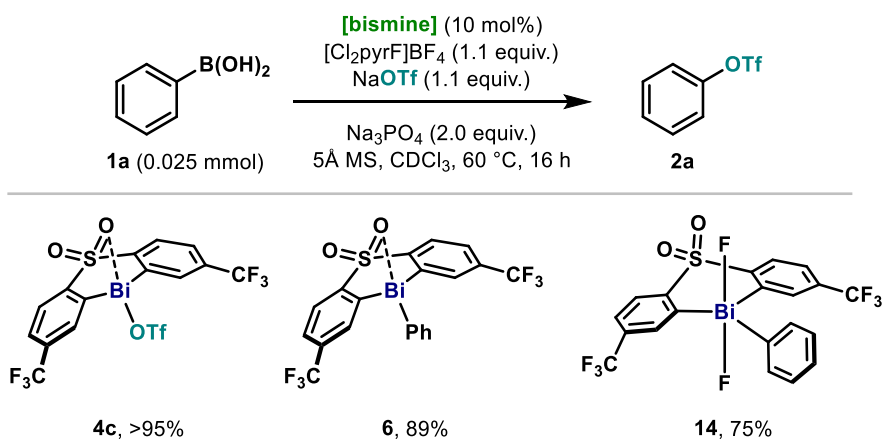
**HRMS (ESI, m/z):** calc'd for C<sub>18</sub>H<sub>9</sub>F<sub>9</sub>O<sub>3</sub>S [M]<sup>+</sup> 476.0123; found 476.0123.

**m.p. (°C):** 68.1 – 68.5.

### 5.5 Catalytic studies using **6** and **14** as catalysts

Phenylbismine **6** and difluoro bismine **14** were tested as catalysts to see if they could be on-cycle intermediates of the Bi-catalyzed coupling of arylboronic acids and NaOTf.

A culture tube equipped with a stir bar was charged with aryl boronic acid (0.025 mmol, 1.0 equiv.), *bismine* (0.0025 mmol, 0.1 equiv.), 1-fluoro-2,6-dichloropyridinium tetrafluoroborate (6.98 mg, 0.0275 mmol, 1.1 equiv.), sodium triflate (4.73 mg, 0.0275 mmol, 1.1 equiv.), sodium phosphate (8.20 mg, 0.050 mmol, 2.0 equiv.), 5Å molecular sieves (10 mg) and dry CDCl<sub>3</sub> (1 mL) under an Ar atmosphere and stirred at 60 °C for 16 h. After the indicated time, the yield was calculated by <sup>19</sup>F NMR using 1-fluoro-4-nitrobenzene (added by weight) as internal standard. Yield was determined by integration of the CF<sub>3</sub> group on the Ar–OTf moiety at a chemical shift ca.  $\delta$  = 73.0 ppm.



These results suggest that **6** and **14** could be used as catalysts. Indeed, phenylbismine **6** is a necessary intermediate after transmetalation to **4c** with phenylboronic acid **2a**, and therefore is proposed to be an on-cycle intermediate. Regarding difluorobismine **14**, this high-valent species could enter the catalytic cycle via ligand exchange with NaOTf, generating the proposed intermediate **7a** (see Figure 3, main text).

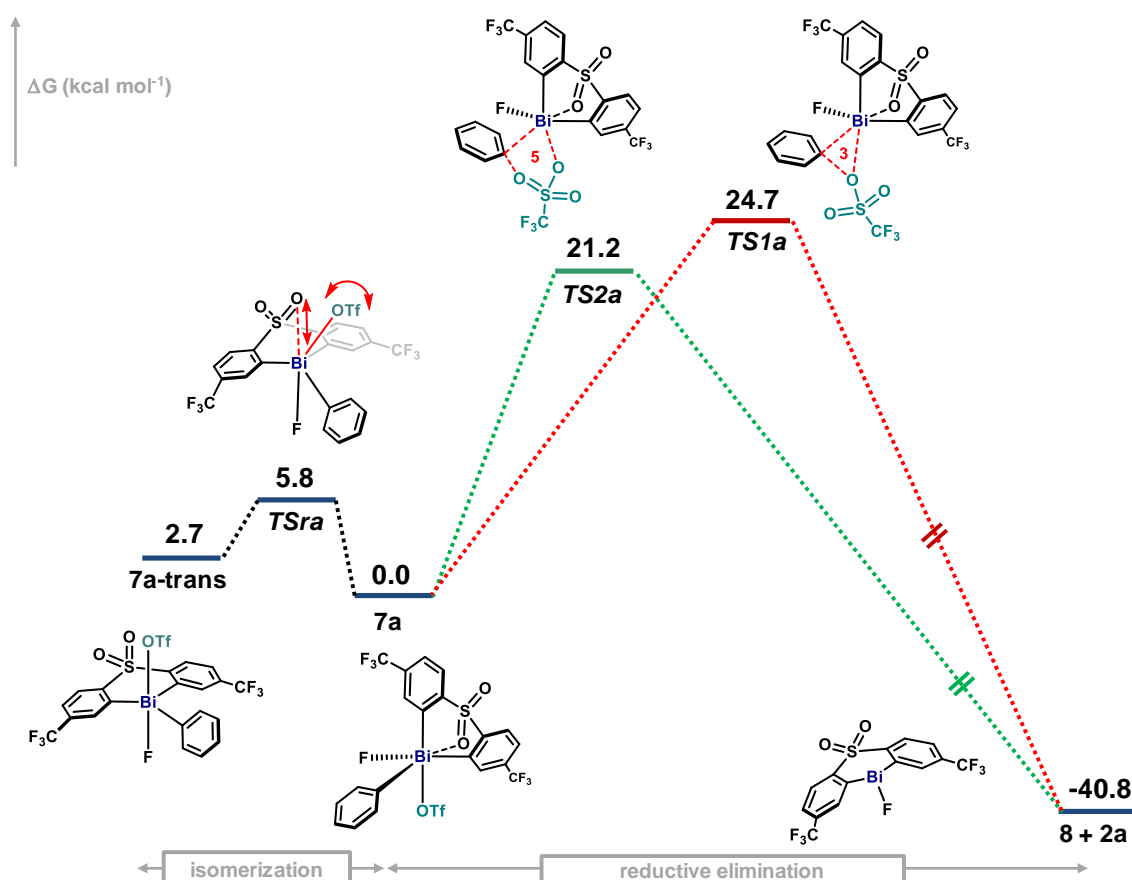


## 6. Computational details

All calculations were performed using the development version of ORCA 4.2.<sup>26-27</sup> Geometries were optimized using the hybrid Perdew-Burke-Ernzerhof functional (PBE0)<sup>28-29</sup> in conjunction with the def2-TZVP basis set,<sup>30</sup> the auxiliary def2/J basis set<sup>31</sup> and the default effective core potential (ECP) for Bi.<sup>32</sup> Fine integration grids (grid6) were applied. The dispersion correction by Grimme<sup>33</sup> with Becke-Johnson damping (D3BJ)<sup>34</sup> as well as the chain of spheres approximation (RIJCOSX)<sup>35</sup> were employed. Subsequent frequency calculations were performed to evaluate enthalpy and entropy corrections at 298.15 K and ensured that all local minima had only real frequencies while a single imaginary frequency confirmed the presence of transition states. Natural bond orbital (NBO) analysis<sup>36</sup> was performed at the PBE0-D3BJ/def2-TZVP level of theory. The Chemcraft software was used to display molecular geometries.<sup>37</sup>

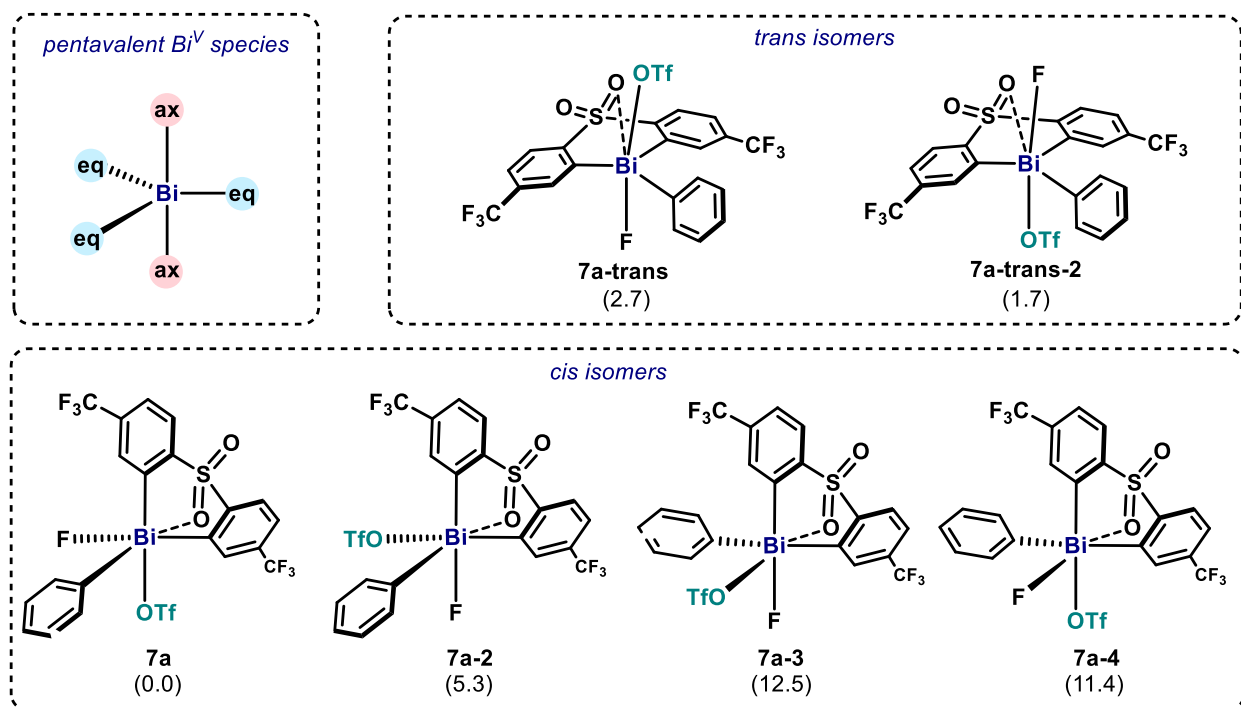
### 6.1 Energy profiles for the reductive elimination step

As stated in the manuscript, DFT studies on the reaction profile starting from **7a** show that two reductive elimination pathways are possible to furnish **2a** together with the corresponding bismine fluoride **8** (Figure S14). However, **7a** could also undergo isomerization to **7a-trans** through a kinetic barrier of  $\Delta G^\ddagger = 5.8$  kcal/mol (**TSra**). The *trans* isomer **7a-trans** is computed to be 2.7 kcal/mol higher in energy than **7a**, being the latter the most stable species. This extra stabilization of the *cis* form is suggested to be a result of the coordination of the  $-\text{SO}_2-$  moiety in **7a**, thus providing electronic density to the highly electrophilic  $\text{Bi}^{\text{V}}$  center.



**Figure S14.** Gibbs energy profile of the reaction from **7a**. Relative Gibbs energy values are given in  $\text{kcal mol}^{-1}$ .

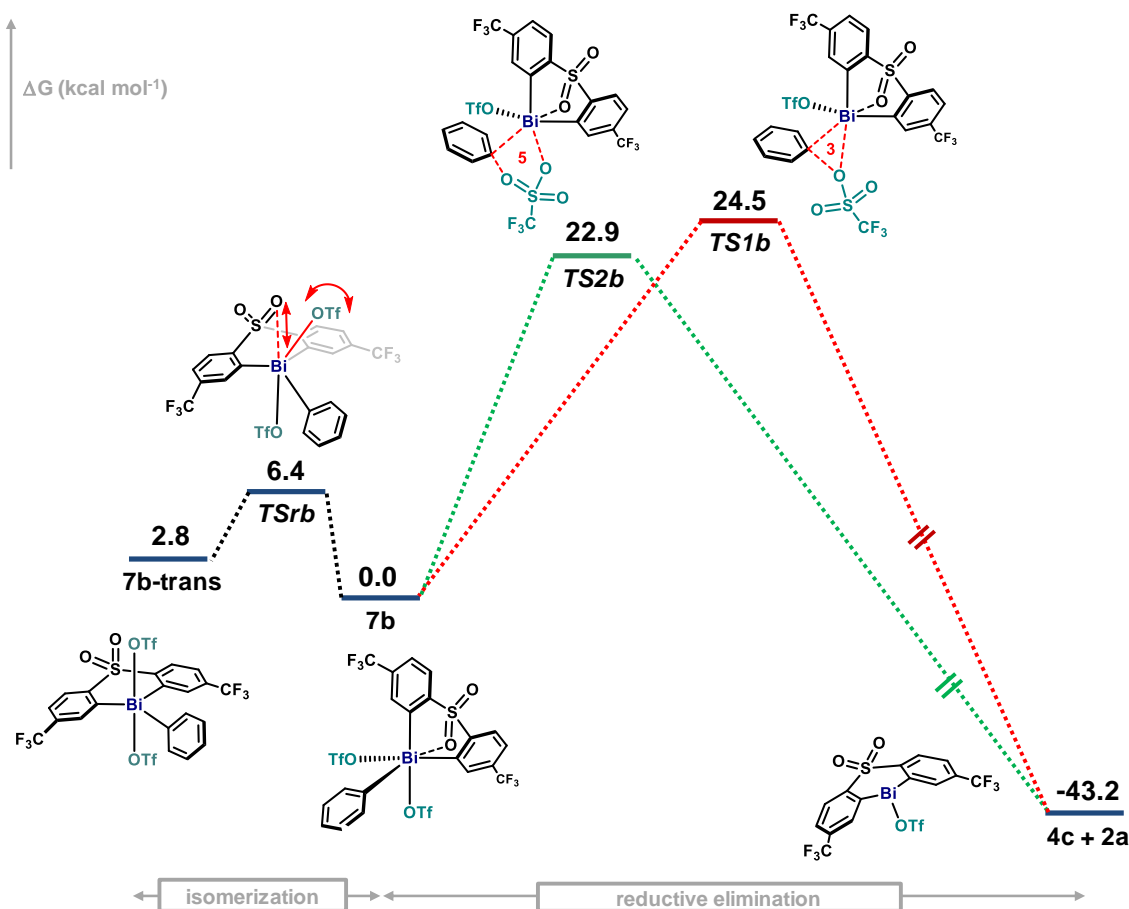
Other isomers were also evaluated (see Figure S15), but **7a** resulted to be the most stable conformer. Bismines locating two phenyl groups in apical were not considered, as they are predicted to be highly energetic and therefore unlikely to be formed according to the polarity rule in pentavalent main-group compounds.<sup>38</sup>



**Figure S15.** Isomers of **7a** evaluated in this study. In parenthesis, relative energies given in kcal mol<sup>-1</sup>.

Then, **7a** can undergo reductive elimination either through a 3-membered ring transition state (**TS1a**,  $\Delta G^\ddagger = 24.7$  kcal/mol) or through a 5-membered ring transition state (**TS2a**,  $\Delta G^\ddagger = 21.2$  kcal/mol). As shown in Figure S13, the 5-membered **TS2a** is slightly favored over the 3-membered **TS1a** ( $\Delta\Delta G^\ddagger = 3.5$  kcal/mol), pointing towards **TS2a** as the preferable pathway for the C–O bond forming event. Furthermore, the reductive elimination from **7a**, which was detected by HRMS (see section 3.3.3), proceeds in less than 10 minutes at room temperature (ca. 22 °C). This result agrees with the theoretical results depicted in Figure S14.

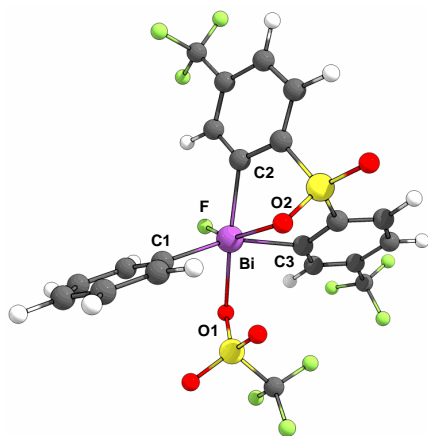
Similar results were obtained when the DFT profile of the reaction starting from ditriflate bismine **7b** was studied (Figure S16). Similarly to **7a**, **7b** can also undergo isomerization via turnstile pseudo-rotation to furnish **7b-trans** ( $\Delta G = 2.8$  kcal/mol) through a kinetic barrier of  $\Delta G^\ddagger = 6.1$  kcal/mol (**TSrb**). In this case, the *cis* isomer is also the most stable form probably due to coordination of the –SO<sub>2</sub>– moiety to the electrophilic Bi(V) center.



**Figure S16.** Gibbs energy profile of the reaction from **7b**. Relative Gibbs energy values are given in kcal mol<sup>-1</sup>.

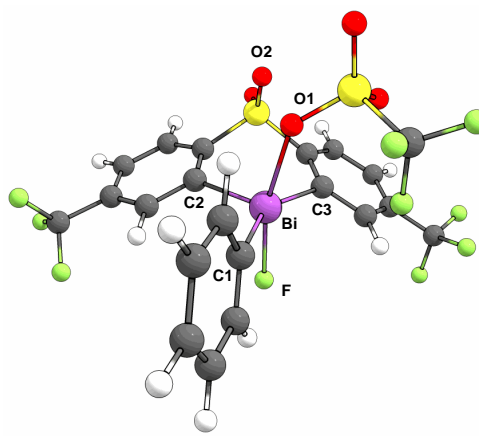
In line with the reactivity observed with **7a**, **7b** could also undergo reductive elimination through two different cyclic transition states. Indeed, a 3-membered ring transition state (**TS1b**) would yield **4c** and **2a** through a kinetic barrier of  $\Delta G^\ddagger = 24.5$  kcal/mol, while a 5-membered transition state (**TS2b**) would yield the same products through a pathway with a lower activation barrier ( $\Delta G^\ddagger = 22.9$  kcal/mol). In this case, although **TS2b** it is slightly favored over **TS1b**, the energetic difference between both routes ( $\Delta\Delta G^\ddagger = 1.6$  kcal/mol) is not sufficient to fully rule out **TS1b**. Also, it is important to note that in both profiles the reaction is highly exergonic (Figures S14 and S16,  $\Delta G = -40.8$  and  $-43.2$  kcal/mol, respectively), showing that this reductive elimination is thermodynamically favored independently of the anions bonded to **7**.

The most relevant structures of the reductive elimination profiles from species **7a** and **7b** are shown in Figures S17 and S18, together with selected structural parameters.



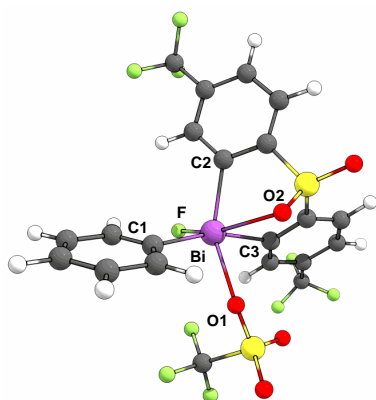
**7a**

Selected distances (Å) and angles (°): Bi-C1 2.184, Bi-C2 2.271, Bi-C3 2.198, Bi-F 2.013, Bi-O1 2.459, Bi-O2 2.674; C1-Bi-C2 108.33, C2-Bi-C3 89.65, C1-Bi-C3 151.33, F-Bi-O1 78.29.



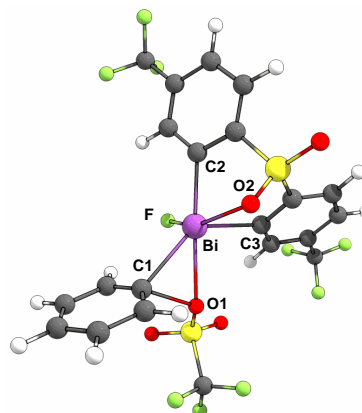
**7a-trans**

Selected distances (Å) and angles (°): Bi-C1 2.196, Bi-C2 2.192, Bi-C3 2.190, Bi-F 2.069, Bi-O1 2.285, Bi-O2 3.495; C1-Bi-C2 111.06, C2-Bi-C3 98.19, C1-Bi-C3 150.32, F-Bi-O1 163.68.



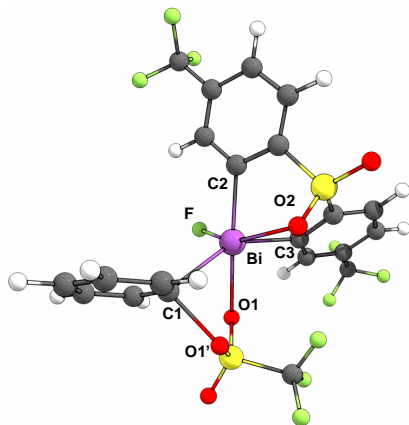
**TSra**

Selected distances (Å) and angles (°): Bi-C1 2.187, Bi-C2 2.259, Bi-C3 2.198, Bi-F 2.030, Bi-O1 2.402, Bi-O2 2.594; C1-Bi-C2 105.78, C2-Bi-C3 90.05, C1-Bi-C3 162.21, F-Bi-O1 122.41.



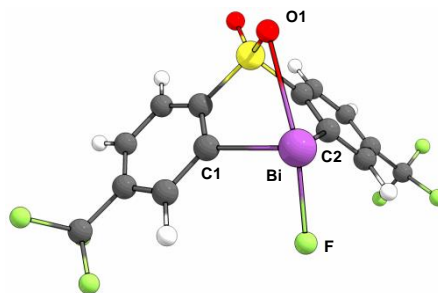
**TS1a**

Selected distances (Å) and angles (°): Bi-C1 2.541, Bi-C2 2.269, Bi-C3 2.240, Bi-F 2.030, Bi-O1 2.578, Bi-O2 2.662, C1-O1 2.128; C1-Bi-C2 136.32, C2-Bi-C3 88.43, C1-Bi-C3 133.83, Bi-C1-O1 66.37.



**TS2a**

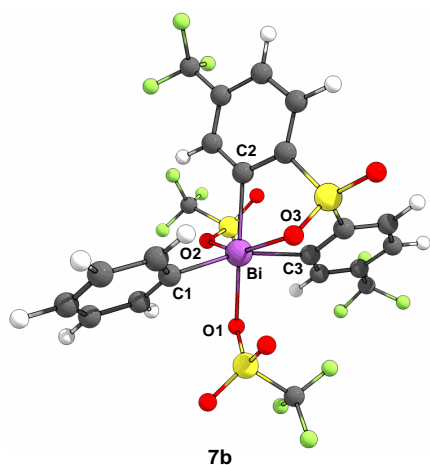
Selected distances (Å) and angles (°): Bi-C1 2.539, Bi-C2 2.269, Bi-C3 2.246, Bi-F 2.029, Bi-O1 2.663, Bi-O2 2.690, C1-O1' 2.044; C1-Bi-C2 116.63, C2-Bi-C3 88.54, C1-Bi-C3 1148.25, F-Bi-O1 79.08, Bi-C1-O1' 53.60.



**8**

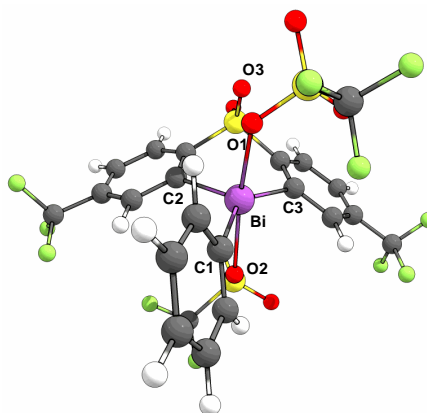
Selected distances (Å) and angles (°): Bi-C1 2.262, Bi-C2 2.259, Bi-F 2.048, Bi-O1 2.679; C1-Bi-C2 86.06, C2-Bi-F 90.14, C1-Bi-F 90.87, F-Bi-O1 154.99.

**Figure S17.** Relevant structures of the reductive elimination profile from species **7a**.



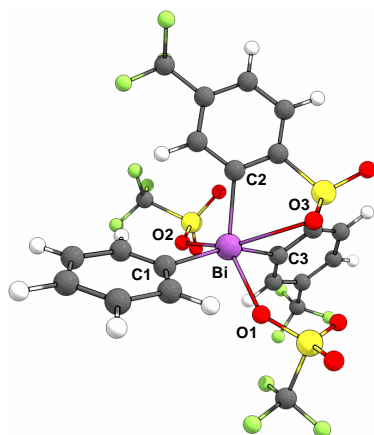
**7b**

Selected distances (Å) and angles (°): Bi-C1 2.181, Bi-C2 2.268, Bi-C3 2.198, Bi-O1 2.472, Bi-O2 2.180, Bi-O3 2.561; C1-Bi-C2 103.93, C2-Bi-C3 91.36, C1-Bi-C3 158.52, O1-Bi-O2 76.08.



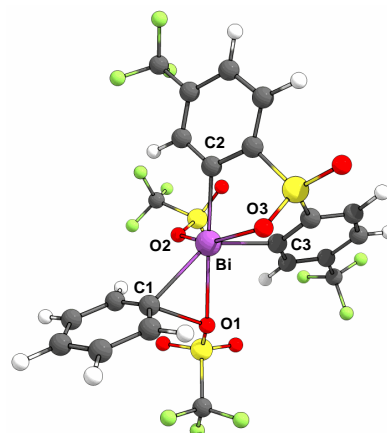
**7b-trans**

Selected distances (Å) and angles (°): Bi-C1 2.201, Bi-C2 2.186, Bi-C3 2.193, Bi-O1 2.207, Bi-O2 2.294, Bi-O3 3.349; C1-Bi-C2 114.50, C2-Bi-C3 99.97, C1-Bi-C3 142.59, O1-Bi-O2 168.74.



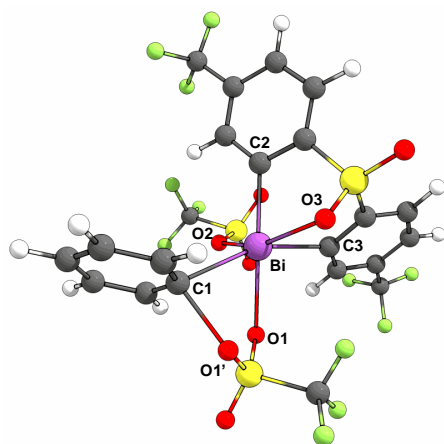
**TSrb**

Selected distances (Å) and angles (°): Bi-C1 2.202, Bi-C2 2.234, Bi-C3 2.202, Bi-O1 2.283, Bi-O2 2.234, Bi-O3 2.677; C1-Bi-C2 105.17, C2-Bi-C3 95.92, C1-Bi-C3 158.57, O1-Bi-O2 129.57.



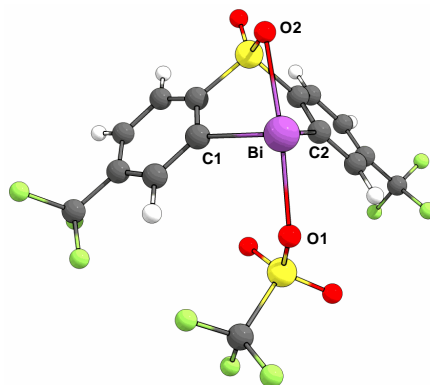
**TS1b**

Selected distances (Å) and angles (°): Bi-C1 2.532, Bi-C2 2.269, Bi-C3 2.235, Bi-O1 2.583, Bi-O2 2.189, Bi-O3 2.527, C1-O1 2.160; C1-Bi-C2 133.51, C2-Bi-C3 90.53, C1-Bi-C3 134.96, Bi-C1-O1 66.24.



**TS2b**

Selected distances (Å) and angles (°): Bi-C1 2.515, Bi-C2 2.271, Bi-C3 2.244, Bi-O1 2.635, Bi-O2 2.085, Bi-O3 2.544, C1-O1' 2.085; C1-Bi-C2 111.27, C2-Bi-C3 89.87, C1-Bi-C3 157.18, Bi-C1-O1' 82.80.



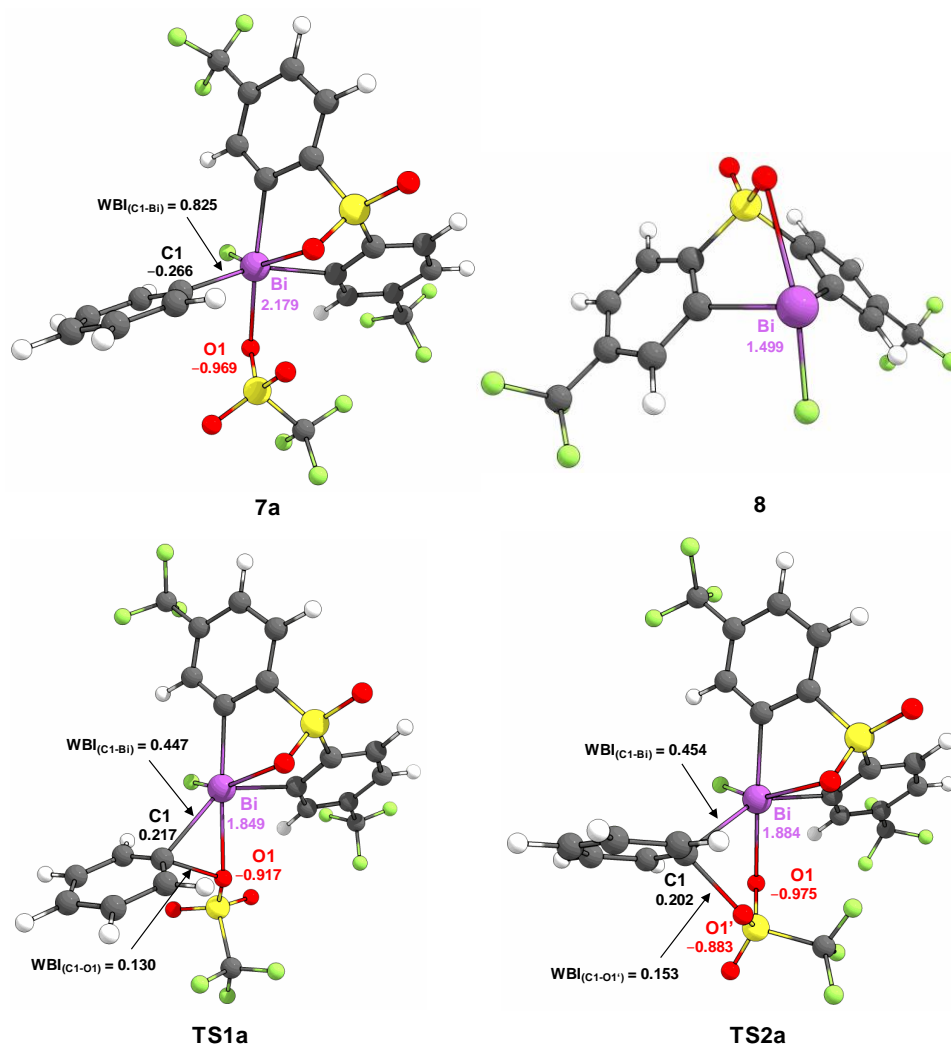
**4c**

Selected distances (Å) and angles (°): Bi-C1 2.264, Bi-C2 2.262, Bi-O1 2.224, Bi-O2 2.494; C1-Bi-C2 86.87, C2-Bi-F 92.29, C1-Bi-F 94.17, O1-Bi-O2 161.84.

**Figure S18.** Relevant structures of the reductive elimination profile from species **7b**.

## 6.2 NBO analysis: Natural charges and Wiberg bond indices of selected species

NBO analysis was performed on the most relevant species involved in the reductive elimination from **7a**, revealing interesting electronic and bonding features of these compounds (Figure S19). As reported in the main text, the natural charge on the Bi center decreased from 2.179 in **7a**, to 1.849 and 1.884 in **TS1a** and **TS2a**, respectively, to finally 1.499 in **8**. This progressive change of charge at the Bi center points out to a concerted reductive elimination. In addition, the C atom directly attached to the Bi center (C1) also experienced a substantial change, becoming positively charged at the transition state (see Figure S19 and Table S8). This buildup of positive charge on the C atom directly bound to the Bi center was also observed experimentally in previous reductive elimination studies from Bi<sup>V</sup> species.<sup>8</sup>



**Figure S19.** Natural charges (C1, O1, O1' and Bi atoms) and Wiberg bond indices (WBI) of selected bonds of species **7a**, **TS1a**, **TS2a** and **8**.

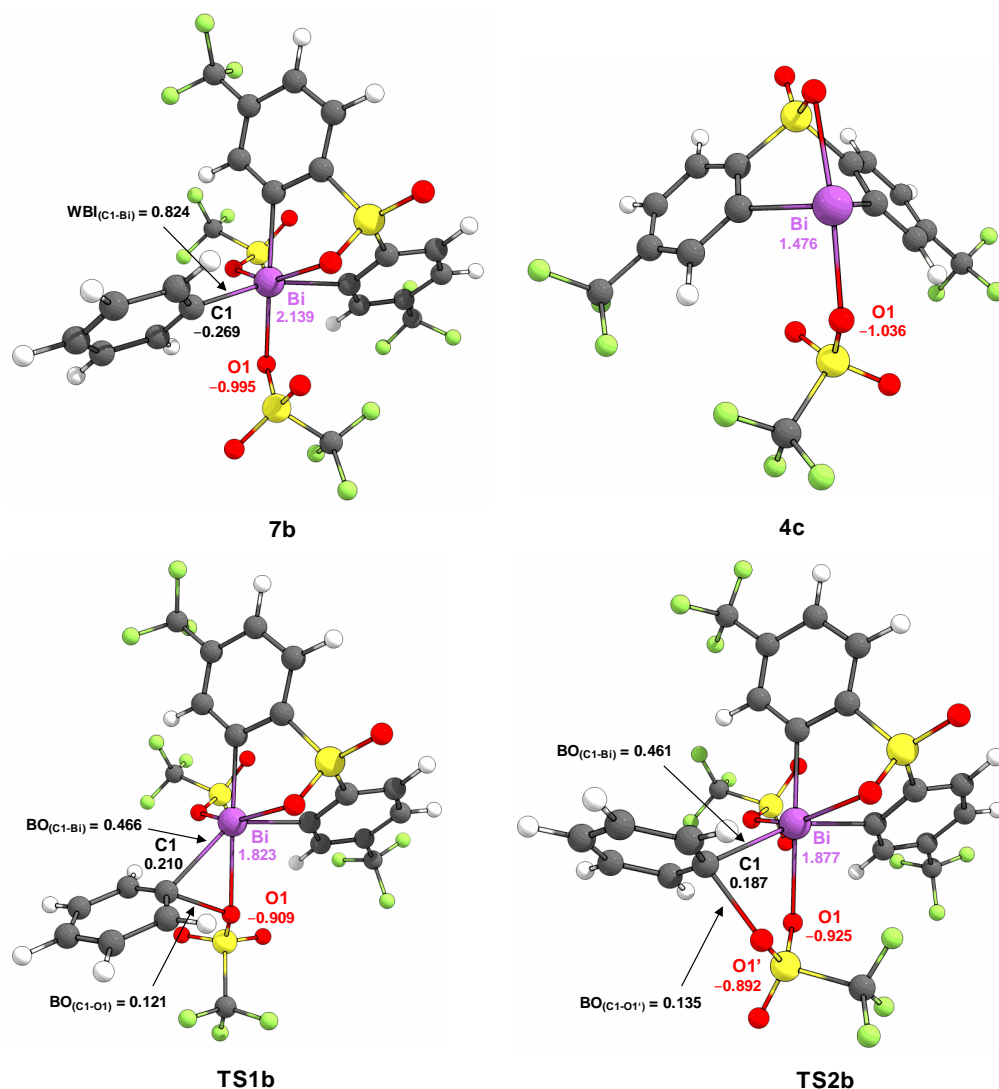
**Table S8.** Relevant Wiberg Bond Indices (WBI) and NPA atomic charges ( $q$ ) for Bi species **7a**, **TS1a**, **TS2a** and **8**.

<b>Compound</b>	<b>WBI<sub>Bi-C1</sub></b>	<b>WBI<sub>C1-O1</sub></b>	<b>WBI<sub>C1-O1'</sub></b>	<b><math>q_{\text{Bi}}</math></b>	<b><math>q_{\text{C1}}</math></b>	<b><math>q_{\text{O1}}</math></b>	<b><math>q_{\text{O1'}}</math></b>
<b>7a</b>	0.826	-	-	2.179	-0.266	-0.969	-0.998
<b>TS1a</b>	0.447	0.130	-	1.849	0.217	-0.917	-0.997
<b>TS2a</b>	0.454	-	0.153	1.884	0.202	-0.975	-0.883
<b>8</b>	-	-	-	1.499	-	-	-

Furthermore, Wiberg bond indices revealed a decrease of bond order for the C1-Bi bond from **7a** to **TS1a** and **TS2a** (See Figure S19 and Table S8). This result, together with the  $\text{WBI} > 0$  for the respective C-O bonds being formed in **TS1a** and **TS2a** (see Figure S19 and Table S9) indicate that the C1-Bi cleavage happens simultaneously with the O1(′)-C1 bond forming event, as expected in a concerted reductive elimination step.



Similar results were obtained when NBO analysis was performed on the most relevant species involved in the reductive elimination from **7b** (see Figure S20 and Table S9).



**Figure S20.** Natural charges (C1, O1, O1' and Bi atoms) and Wiberg bond indices (WBI) of selected bonds of species **7b**, **TS1b**, **TS2b** and **4c**.

**Table S9.** Relevant Wiberg Bond Indices (WBI) and NPA atomic charges ( $q$ ) for Bi species **7b**, **TS1b**, **TS2b** and **4c**.

Compound	WBI <sub>Bi-C1</sub>	WBI <sub>C1-O1</sub>	WBI <sub>C1-O1'</sub>	$q_{Bi}$	$q_{C1}$	$q_{O1}$	$q_{O1'}$
<b>7b</b>	0.824	-	-	2.139	-0.269	-0.995	-0.998
<b>TS1b</b>	0.461	0.121	-	1.823	0.210	-0.909	-0.972
<b>TS2b</b>	0.466	-	0.135	1.877	0.187	-0.925	-0.892
<b>4c</b>	-	-	-	1.476	-	-1.036	-

### 6.3 XYZ coordinates of DFT optimized structures

#### Coordinates for **7a**

Bi	3.823104	4.282635	6.326739
S	6.755348	3.015195	6.044236
O	6.396986	4.042056	7.010698
C	5.083947	4.350484	4.438985
C	6.313151	3.701845	4.484648
C	7.144787	3.587312	3.385052
H	8.094756	3.074014	3.468816
C	6.728730	4.154738	2.191231
H	7.356044	4.093147	1.311449
C	5.496033	4.788267	2.119580
C	4.666318	4.885204	3.234350
H	3.694792	5.357179	3.148069
C	4.228623	2.129807	6.503834
C	5.543496	1.748058	6.275947
C	5.892030	0.409285	6.228926
H	6.924752	0.127747	6.064395
C	4.900507	-0.542058	6.409896
H	5.150118	-1.595200	6.380913
C	3.586081	-0.150701	6.621335
C	3.232703	1.194594	6.667983
H	2.208544	1.497948	6.840959
C	3.746112	6.294550	7.174010
C	4.816991	6.771404	7.900831
H	5.698971	6.170946	8.078458
C	4.696532	8.048437	8.431892
H	5.510565	8.455441	9.019533
C	3.539740	8.787052	8.229950
H	3.454328	9.777449	8.660837
C	2.485067	8.264129	7.497600
H	1.577464	8.838147	7.355499
C	2.574960	6.989633	6.953042
H	1.750718	6.553725	6.402057
O	8.067947	2.451986	6.011501
C	5.063994	5.408292	0.816729
F	5.452331	6.688667	0.741274
F	5.595182	4.772124	-0.232637
F	3.737505	5.387797	0.673731
C	2.536837	-1.209545	6.849592
F	1.307238	-0.746982	6.628373
F	2.727512	-2.264660	6.047729
F	2.581739	-1.661083	8.107199
S	2.665388	3.989094	9.293556
F	2.644804	2.495548	11.431278
F	0.804020	2.447573	10.304792
F	2.532146	1.373911	9.592928
O	2.045772	3.799677	7.955506
O	4.107188	3.866975	9.181085
O	2.142341	5.084853	10.042444
C	2.125597	2.482888	10.212493
F	2.180117	4.333562	5.165353

#### Coordinates for **7a-trans**

Bi	3.648464	3.819947	6.506694
S	6.372482	1.727138	5.852309
O	6.722617	2.276634	7.126472
C	5.278204	4.149080	5.078180
C	6.165658	3.123148	4.768171
C	7.019644	3.234301	3.684603
H	7.699436	2.422112	3.459676
C	6.998749	4.390215	2.916032
H	7.665464	4.490287	2.069240
C	6.120120	5.413158	3.228936
C	5.243328	5.290442	4.302123
H	4.535857	6.086285	4.508975
C	3.633148	1.630800	6.463552
C	4.768689	0.963735	6.019561
C	4.711803	-0.404925	5.804081
H	5.599828	-0.917887	5.457650
C	3.536864	-1.094654	6.054769
H	3.498105	-2.166351	5.909684
C	2.415343	-0.413785	6.497026
C	2.449767	0.962161	6.682709
H	1.559372	1.484328	7.007495
C	2.736650	5.722807	7.115597
C	3.353144	6.496477	8.083289
H	4.225867	6.146170	8.616410
C	2.798937	7.739055	8.360225
H	3.261214	8.367412	9.111990
C	1.665887	8.169523	7.685587
H	1.241655	9.140287	7.913028
C	1.073542	7.367258	6.722247
H	0.188195	7.704307	6.196527
C	1.610651	6.122720	6.417957
H	1.173325	5.487285	5.659414
F	2.228732	3.671581	5.008762
O	7.223540	0.783368	5.190284
C	6.116805	6.693007	2.437113
F	6.797231	7.652366	3.078883
F	6.677599	6.540433	1.236678
F	4.873673	7.149936	2.251229
C	1.123574	-1.147215	6.742372
F	0.454767	-0.628830	7.775856
F	0.317086	-1.073683	5.674690
F	1.329845	-2.440912	6.996762
O	4.694976	3.895935	8.536966
S	4.660386	2.887465	9.654702
O	4.532243	1.541758	9.188171
O	5.604787	3.211381	10.668173
C	2.996660	3.254283	10.360793
F	2.697967	2.397619	11.319759
F	2.923934	4.487902	10.843082
F	2.068742	3.139108	9.389474

### Coordinates for TSra

Bi	3.332187	4.155422	6.490753
S	6.377708	3.325794	6.297002
O	5.813390	4.287985	7.236981
C	4.610471	4.460058	4.653117
C	5.902731	3.953213	4.719877
C	6.760683	3.945608	3.635353
H	7.762966	3.546729	3.732309
C	6.304767	4.480169	2.439573
H	6.954459	4.508920	1.574282
C	5.014631	4.984276	2.353110
C	4.158296	4.968555	3.451293
H	3.149506	5.351350	3.351456
C	3.997874	2.064493	6.609565
C	5.367351	1.888475	6.476530
C	5.919825	0.619175	6.480076
H	6.991837	0.497528	6.387575
C	5.074602	-0.469158	6.625461
H	5.483661	-1.470857	6.655272
C	3.705223	-0.281208	6.741876
C	3.146305	0.992368	6.730665
H	2.078783	1.126690	6.841479
C	2.594387	6.140331	7.037951
C	3.200113	6.836551	8.064996
H	3.977764	6.391980	8.670535
C	2.738731	8.121912	8.314056
H	3.185009	8.696289	9.116939
C	1.708158	8.659314	7.555331
H	1.352459	9.660655	7.766648
C	1.122004	7.922933	6.537318
H	0.308430	8.340048	5.955917
C	1.567302	6.636086	6.258810
H	1.105290	6.037495	5.483797
O	7.762601	2.981521	6.330815
C	4.508545	5.507251	1.034495
F	5.494373	6.016839	0.290663
F	3.936150	4.529446	0.320083
F	3.591266	6.464037	1.202222
C	2.803308	-1.483863	6.850920
F	1.657399	-1.194008	7.460958
F	2.501216	-1.957913	5.631875
F	3.390588	-2.476503	7.524150
S	2.883940	3.063586	9.924162
F	0.402016	2.397472	10.492360
F	0.663629	4.481059	10.002593
F	0.728474	2.993895	8.440683
O	3.356820	4.023599	8.888719
O	3.140873	1.694977	9.577768
O	3.172824	3.509582	11.248410
C	1.061081	3.245577	9.720771
F	1.687025	3.697065	5.392599

### Coordinates for TS1a

Bi	3.597016	4.891890	5.395243
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S	6.667185	4.172670	4.785881
O	6.177522	4.749154	6.033909
C	4.793726	5.736986	3.663032
C	6.096459	5.275384	3.530397
C	6.899360	5.618426	2.456975
H	7.909885	5.234671	2.387070
C	6.377791	6.468539	1.493127
H	6.984683	6.771656	0.649867
C	5.074370	6.929909	1.609250
C	4.271976	6.561836	2.686632
H	3.247271	6.909963	2.744317
C	4.311041	2.850648	4.812223
C	5.669739	2.736792	4.537571
C	6.233049	1.554158	4.095779
H	7.296460	1.497564	3.898501
C	5.404145	0.453851	3.929866
H	5.813547	-0.486995	3.587090
C	4.049099	0.559136	4.201327
C	3.488485	1.754494	4.651668
H	2.428966	1.806780	4.879867
C	2.420053	5.825712	7.444109
C	3.209181	6.027992	8.537700
H	4.081182	5.431049	8.763382
C	2.797237	7.078410	9.356754
H	3.381783	7.301990	10.241500
C	1.662370	7.814487	9.051128
H	1.352832	8.620608	9.704255
C	0.911118	7.513574	7.925419
H	0.011641	8.071355	7.692916
C	1.276780	6.468410	7.077589
H	0.685328	6.176255	6.220667
O	8.054218	3.871500	4.614191
C	4.486894	7.800067	0.529787
F	3.639246	8.702386	1.033384
F	5.429810	8.464092	-0.145443
F	3.803415	7.066784	-0.358126
C	3.143901	-0.633414	4.022123
F	3.761518	-1.633190	3.381012
F	2.728511	-1.109197	5.197788
F	2.060161	-0.310775	3.312056
S	0.824355	3.027945	7.385226
F	1.144178	3.607511	9.919996
F	-0.112306	1.892469	9.547095
F	2.027667	1.731715	9.325212
O	0.784183	1.808986	6.637469
O	2.140653	3.732944	7.179685
O	-0.290127	3.921311	7.339619
C	0.980155	2.529936	9.154349
F	1.921222	4.965906	4.251114

### Coordinates for TS2a

Bi	3.816367	4.154540	6.438287
S	6.699746	2.735807	6.151469
O	6.344457	3.666279	7.215681
C	5.177881	4.338723	4.632528

C	6.360295	3.612418	4.658065
C	7.221604	3.545142	3.575675
H	8.134156	2.965080	3.638743
C	6.886481	4.248648	2.430218
H	7.545666	4.235151	1.571349
C	5.700505	4.970763	2.382533
C	4.838355	5.012946	3.473323
H	3.903736	5.556627	3.406364
C	4.123232	1.930324	6.370696
C	5.433316	1.500299	6.204438
C	5.757238	0.156935	6.133826
H	6.789749	-0.146798	6.012414
C	4.736700	-0.774243	6.254951
H	4.962082	-1.832391	6.227903
C	3.427808	-0.350517	6.433058
C	3.108274	1.003825	6.486181
H	2.084198	1.320479	6.643593
C	3.493491	6.248085	7.838358
C	4.673636	6.884492	8.109857
H	5.569528	6.351500	8.397269
C	4.635976	8.270763	7.991318
H	5.544159	8.830180	8.183156
C	3.461763	8.924672	7.645772
H	3.448431	10.004354	7.567965
C	2.303402	8.201163	7.409209
H	1.381241	8.703876	7.142105
C	2.290724	6.811091	7.512648
H	1.397912	6.228234	7.330220
O	7.994448	2.129205	6.110157
C	5.323699	5.669881	1.103551
F	6.390340	6.214469	0.506233
F	4.779349	4.812331	0.229290
F	4.435729	6.644930	1.308952
C	2.321503	-1.366161	6.547362
F	1.356784	-0.952450	7.370358
F	1.755778	-1.598330	5.354733
F	2.771642	-2.538346	7.006262
S	2.159621	3.974549	9.414389
F	3.266804	2.772454	11.465337
F	2.025939	1.500970	10.239226
F	3.982073	2.091335	9.547106
O	1.812613	3.519030	8.072924
O	3.323749	4.896487	9.362687
O	1.083564	4.384517	10.249873
C	2.906947	2.490482	10.224884
F	2.229245	4.328462	5.186563

#### Coordinates for **8**

Bi	5.978942	5.086037	4.213839
S	7.131588	2.208083	5.169393
O	7.699682	0.993588	5.668996
C	7.017462	3.587017	2.875520
C	7.422170	2.385089	3.437232
C	7.997466	1.362923	2.701102
H	8.286562	0.437409	3.184060

C	8.199382	1.569189	1.346743
H	8.656437	0.797046	0.740234
C	7.804451	2.767366	0.763878
C	7.207111	3.772470	1.516392
H	6.877295	4.682815	1.030564
C	4.718830	3.348703	4.919707
C	5.368919	2.172715	5.263537
C	4.697179	1.020419	5.635512
H	5.248338	0.123508	5.890279
C	3.314369	1.061211	5.689628
H	2.754611	0.187074	5.997953
C	2.643045	2.230167	5.353393
C	3.334517	3.369728	4.956629
H	2.787240	4.259849	4.669692
O	7.507321	3.497502	5.736287
C	8.063711	2.973144	-0.704287
F	9.366587	3.193838	-0.935417
F	7.718616	1.895769	-1.419995
F	7.392208	4.015681	-1.196123
C	1.138740	2.228412	5.394855
F	0.631916	3.462541	5.417061
F	0.623996	1.603725	4.326617
F	0.683402	1.586477	6.478569
F	4.607858	5.491641	2.748073

#### Coordinates for **7b**

Bi	3.861488	4.234607	6.445433
S	6.704085	2.908307	6.148038
O	6.314652	3.934600	7.114869
C	5.132043	4.364395	4.571760
C	6.313389	3.635206	4.595525
C	7.138882	3.504111	3.491981
H	8.054011	2.928425	3.555997
C	6.767184	4.150366	2.324769
H	7.394072	4.085005	1.444357
C	5.592766	4.891864	2.285553
C	4.767531	4.997278	3.399271
H	3.847180	5.562905	3.334297
C	4.166381	2.061332	6.564989
C	5.474119	1.657731	6.340489
C	5.790490	0.311912	6.267306
H	6.817891	0.007657	6.110439
C	4.773196	-0.616140	6.421865
H	4.997737	-1.674769	6.385475
C	3.466847	-0.196492	6.630340
C	3.142730	1.154000	6.699732
H	2.121019	1.472240	6.862126
C	3.709238	6.302616	7.120745
C	4.889261	7.013039	7.207670
H	5.850078	6.558914	6.998292
C	4.797008	8.340338	7.604358
H	5.700980	8.929735	7.699041
C	3.559071	8.900481	7.885481
H	3.498657	9.935952	8.198218
C	2.399240	8.147901	7.778523

H	1.435962	8.587644	8.006132
C	2.458778	6.815040	7.392201
H	1.565748	6.207568	7.327954
O	8.015051	2.344195	6.161705
C	5.190425	5.548655	0.990569
F	4.285267	6.510098	1.179376
F	6.243866	6.099722	0.375139
F	4.661379	4.657622	0.144545
C	2.379514	-1.234691	6.757302
F	1.269118	-0.732031	7.286995
F	2.069056	-1.745239	5.560378
F	2.779161	-2.253317	7.528890
O	2.082110	4.366559	5.193030
S	2.615437	3.951599	9.341535
O	2.600571	2.555265	3.652386
O	0.540336	2.478083	5.009337
C	0.659057	4.249086	3.065854
F	2.715291	2.441023	11.462425
F	0.952528	2.144560	10.253082
F	2.850242	1.345481	9.611558
O	2.001638	3.755020	8.002164
S	1.539546	3.234470	4.332838
O	4.063284	3.977152	9.192103
O	2.002369	4.964005	10.136357
C	2.256688	2.369654	10.222832
F	0.106603	3.438766	2.179634
F	-0.281206	4.985659	3.633379
F	1.515609	5.052109	2.441354

#### Coordinates for **7b-trans**

Bi	3.301499	4.007716	6.519554
S	6.255429	2.338434	6.023109
O	6.432619	3.067291	7.244496
C	4.828238	4.479609	5.027630
C	5.853673	3.568210	4.807265
C	6.665603	3.684984	3.694653
H	7.454777	2.961024	3.536579
C	6.456347	4.731973	2.809824
H	7.085997	4.833024	1.934732
C	5.436187	5.641714	3.035194
C	4.602180	5.511581	4.139917
H	3.779102	6.203036	4.275702
C	3.590461	1.840534	6.686078
C	4.804257	1.330624	6.247171
C	4.937163	-0.037231	6.065668
H	5.885514	-0.429735	5.721814
C	3.863374	-0.871192	6.325664
H	3.962997	-1.939764	6.180372
C	2.657330	-0.342521	6.758487
C	2.506618	1.025518	6.933465
H	1.547802	1.424795	7.234771
C	1.823520	5.604961	6.849672
C	2.248801	6.692755	7.593239
H	3.225360	6.719358	8.055932
C	1.368913	7.755909	7.742362

H	1.680397	8.620379	8.316088
C	0.108249	7.708843	7.166651
H	-0.572114	8.542808	7.290840
C	-0.287041	6.600791	6.433226
H	-1.272485	6.562970	5.984715
C	0.575007	5.525467	6.258952
H	0.279748	4.669049	5.670618
O	7.288889	1.505975	5.488479
C	5.247765	6.793083	2.082666
F	6.121399	7.775939	2.340561
F	5.439058	6.417941	0.815591
F	4.023573	7.318029	2.173328
C	1.503606	-1.278680	7.015787
F	0.398709	-0.627738	7.381815
F	1.213598	-1.996876	5.928433
F	1.803693	-2.145062	7.991875
O	1.881961	3.401554	4.822797
S	4.557605	3.911481	9.625208
O	3.448085	2.162278	3.427235
O	1.172885	1.297925	3.834744
C	1.437733	3.414786	2.298746
F	3.254670	4.050127	11.884734
F	3.337436	5.918427	10.808780
F	2.025979	4.344776	10.132748
O	4.303999	4.709106	8.355825
S	2.063818	2.404388	3.709321
O	4.210467	2.533884	9.455341
O	5.780064	4.295656	10.235568
C	3.214668	4.602017	10.685110
F	1.496420	2.712599	1.179792
F	0.180131	3.783027	2.513308
F	2.178827	4.512337	2.156961

#### Coordinates for **TSrb**

Bi	3.240192	4.137819	6.437532
S	6.199487	2.967460	6.235491
O	5.780033	3.919404	7.253705
C	4.657455	4.571129	4.766349
C	5.818887	3.815546	4.738503
C	6.658504	3.809061	3.638913
H	7.565139	3.216889	3.648435
C	6.319361	4.598334	2.551025
H	6.961165	4.622033	1.678815
C	5.163948	5.368835	2.579827
C	4.321050	5.355783	3.683812
H	3.414994	5.947300	3.674096
C	3.681157	1.983859	6.556440
C	5.016560	1.661536	6.365480
C	5.426305	0.342393	6.407792
H	6.473748	0.102218	6.275138
C	4.484739	-0.640546	6.671544
H	4.791856	-1.675733	6.744192
C	3.156223	-0.301780	6.870964
C	2.731752	1.021948	6.799069
H	1.688890	1.266942	6.950978

C	2.204747	6.042859	6.823821	H	5.819239	-0.519259	3.549929
C	2.561919	6.775560	7.940712	C	4.053530	0.493168	4.216464
H	3.220346	6.372713	8.697509	C	3.477524	1.679780	4.665110
C	2.018176	8.047314	8.069948	H	2.422695	1.707981	4.915230
H	2.273760	8.641057	8.939344	C	2.431746	5.809156	7.403989
C	1.158398	8.548919	7.104594	C	3.269974	6.063469	8.449240
H	0.740859	9.542169	7.218393	H	4.178228	5.509339	8.639056
C	0.826649	7.785704	5.996008	C	2.853975	7.107416	9.274803
H	0.149532	8.172220	5.243767	H	3.473820	7.370481	10.123907
C	1.356843	6.511637	5.836430	C	1.672193	7.786340	9.019867
H	1.086646	5.906729	4.982533	H	1.360595	8.587682	9.677848
O	7.522715	2.434471	6.196664	C	0.876829	7.433764	7.940756
C	4.816274	6.204029	1.374791	H	-0.060153	7.943815	7.750704
F	5.818811	7.028783	1.049858	C	1.243650	6.392294	7.087704
F	4.577296	5.435187	0.307273	H	0.611712	6.053127	6.278747
F	3.731549	6.953594	1.583329	O	7.997902	3.893999	4.603224
C	2.147418	-1.386875	7.156714	C	4.458963	7.961064	0.615399
F	1.121223	-0.927508	7.873152	F	3.651712	8.868439	1.174469
F	1.652246	-1.896061	6.024726	F	5.415586	8.623333	-0.042731
F	2.701491	-2.395934	7.836392	F	3.739488	7.292514	-0.291112
O	1.585066	3.664151	5.014347	C	3.195060	-0.744195	4.117961
S	3.832937	3.305167	9.863025	F	3.689932	-1.609822	3.223028
O	2.957781	2.387129	3.456343	F	3.144098	-1.379856	5.294357
O	0.758252	1.529388	4.189134	F	1.950447	-0.453060	3.758020
C	0.800168	3.604937	2.572380	O	1.727274	4.915507	4.245226
F	2.529841	2.115386	11.783207	S	0.897272	2.951427	7.444423
F	1.578027	3.916183	11.067966	O	2.511745	3.950448	2.151039
F	1.494906	2.111813	9.888061	O	0.590986	2.953120	3.344835
O	3.256922	4.098071	8.719888	C	0.244466	5.293978	2.189246
S	1.619971	2.627425	3.906990	F	1.047451	3.887024	9.887607
O	4.413471	2.064731	9.449028	F	-0.139102	2.095204	9.685611
O	4.531150	4.147618	10.777319	F	2.013989	1.978470	9.614505
C	2.260728	2.836450	10.705981	O	0.932111	1.642033	6.872489
F	0.651670	2.853585	1.497259	S	1.377538	4.090466	3.012322
F	-0.386245	4.037552	2.975877	O	2.202650	3.669318	7.213390
F	1.547564	4.663317	2.258328	O	-0.232887	3.797312	7.217422
Coordinates for <b>TS1b</b>				C	0.959037	2.708240	9.271734
Bi	3.598214	4.834985	5.379389	F	-0.230100	4.752451	1.081572
S	6.600760	4.159365	4.730082	F	-0.761597	5.612289	2.987605
O	6.061687	4.720938	5.975731	F	0.908014	6.405262	1.875527
C	4.738434	5.748506	3.643985	Coordinates for <b>TS2b</b>			
C	6.034778	5.277321	3.491185	Bi	3.917148	4.029160	6.572899
C	6.839094	5.647102	2.427910	S	6.655329	2.531810	6.120196
H	7.845505	5.256266	2.341133	O	6.307381	3.442121	7.216702
C	6.325227	6.540935	1.500863	C	5.189661	4.266671	4.707280
H	6.931802	6.866177	0.665790	C	6.332924	3.477384	4.669584
C	5.033461	7.025762	1.647710	C	7.165806	3.413234	3.567825
C	4.229267	6.628507	2.712194	H	8.043361	2.778541	3.579251
H	3.215973	7.002511	2.787811	C	6.850453	4.195528	2.466640
C	4.283993	2.793044	4.782045	H	7.483389	4.180933	1.589427
C	5.636305	2.707144	4.476364	C	5.716791	4.993573	2.488749
C	6.212584	1.533546	4.025520	C	4.877446	5.028664	3.599881
H	7.271241	1.495394	3.800617	H	3.979694	5.634860	3.574959
C	5.401475	0.416566	3.897388	C	4.075400	1.797772	6.390630

C	5.360838	1.333185	6.143193
C	5.623349	-0.008563	5.939486
H	6.636561	-0.343650	5.754584
C	4.562626	-0.901301	6.000248
H	4.735025	-1.958684	5.850403
C	3.280392	-0.440815	6.254209
C	3.021369	0.914261	6.456171
H	2.010089	1.255344	6.645872
C	3.540833	6.241626	7.708628
C	4.701537	6.949603	7.853668
H	5.635646	6.492457	8.149898
C	4.591581	8.312795	7.591195
H	5.479900	8.927837	7.675010
C	3.372700	8.872746	7.236798
H	3.304025	9.935906	7.044667
C	2.240115	8.079921	7.137703
H	1.282948	8.510444	6.867884
C	2.297882	6.709740	7.389457
H	1.426260	6.073744	7.318036
O	7.940492	1.910471	6.074618
C	5.374203	5.863959	1.308528
F	5.567049	7.158966	1.601587
F	6.123654	5.582683	0.239978
F	4.094776	5.727730	0.954706
C	2.124082	-1.404893	6.338621
F	1.100749	-1.000438	5.587693
F	2.467747	-2.631590	5.933367
F	1.682116	-1.508609	7.597701
O	2.116838	4.349470	5.359664
S	2.389739	4.044160	9.593600
O	2.489890	2.809385	3.508067
O	0.503253	2.565229	4.953732
C	0.593649	4.635704	3.332481
F	3.802027	3.053188	11.570631
F	2.500756	1.634242	10.595427
F	4.318111	2.276968	9.623749
O	2.001126	3.488081	8.299565
S	1.497109	3.393455	4.356176
O	3.463151	5.052947	9.420033
O	1.335249	4.405519	10.476008
C	3.309284	2.664435	10.407434
F	-0.064054	4.011429	2.370623
F	-0.265381	5.315338	4.078686
F	1.450583	5.492592	2.784184

#### Coordinates for **4c**

Bi	5.774046	4.999644	3.976059
S	6.841866	2.170200	4.845344
O	7.447768	0.999927	5.394900
C	6.765371	3.539913	2.557762
C	7.147793	2.331565	3.120015
C	7.691055	1.290647	2.385896
H	7.964895	0.361301	2.870159
C	7.877509	1.485391	1.028547
H	8.299297	0.696832	0.417897

C	7.512737	2.693692	0.446929
C	6.957993	3.721510	1.199617
H	6.656521	4.636801	0.708133
C	4.428203	3.290390	4.597166
C	5.083620	2.112347	4.926746
C	4.421436	0.946891	5.270784
H	4.977506	0.049979	5.514659
C	3.038569	0.977804	5.314625
H	2.482447	0.093096	5.598412
C	2.361995	2.150550	5.004536
C	3.043652	3.305981	4.636471
H	2.480735	4.192891	4.370787
O	7.174583	3.494764	5.388612
C	7.748513	2.882158	-1.028663
F	9.047928	3.105187	-1.279501
F	7.398856	1.793275	-1.722020
F	7.066060	3.914729	-1.521221
C	0.855903	2.134665	5.052160
F	0.338202	3.361141	5.073177
F	0.345788	1.493791	3.994992
F	0.420711	1.493302	6.146717
O	4.308836	5.722294	2.466466
S	3.380364	4.999569	1.514915
O	3.871663	3.698827	1.176995
O	2.013871	5.162119	1.891040
C	3.628602	6.049978	0.015977
F	3.236033	7.293239	0.245744
F	4.917995	6.069424	-0.321583
F	2.933924	5.554097	-0.993991

#### Coordinates for **2a**

C	1.885310	5.996437	5.799661
C	1.240423	4.990278	6.491877
C	2.836995	6.807028	6.387096
C	1.570901	4.782633	7.821737
C	3.161924	6.580450	7.715996
C	2.533454	5.572770	8.432614
H	0.492111	4.388746	5.991497
H	3.317030	7.588149	5.813948
H	1.073559	3.998304	8.379201
H	3.910699	7.201610	8.192278
H	2.791707	5.405393	9.471142
O	1.472486	6.222435	4.476641
S	2.437582	6.020783	3.242436
O	3.787397	6.285461	3.593641
O	1.786554	6.631300	2.144201
C	2.304068	4.190307	2.999480
F	2.794844	3.552718	4.050911
F	1.038909	3.843009	2.833041
F	2.997476	3.859959	1.924933

#### Coordinates for **7a-2**

Bi	3.575253	4.320784	6.128479
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S	6.647742	3.226642	5.683471
O	6.363523	4.293266	6.627079
C	4.748872	4.443224	4.18524
C	5.990467	3.818624	4.15557
C	6.746632	3.742712	2.99687
H	7.712523	3.252993	3.014513
C	6.250929	4.328646	1.84376
H	6.826135	4.295775	0.926708
C	5.022957	4.975014	1.87005
C	4.266063	5.032389	3.034434
H	3.308179	5.531132	3.031786
C	4.271489	2.250417	6.524412
C	5.572598	1.919969	6.167497
C	6.034624	0.618339	6.25801
H	7.057234	0.389348	5.985164
C	5.17126	-0.35898	6.72788
H	5.509269	-1.38318	6.817619
C	3.871333	-0.02684	7.079814
C	3.402911	1.27898	6.972416
H	2.381144	1.532938	7.221498
C	3.795182	6.212779	7.196083
C	2.798087	6.574598	8.083577
H	1.950768	5.924002	8.257609
C	2.927457	7.792681	8.737937
H	2.16263	8.102613	9.439945
C	4.025566	8.605035	8.495882
H	4.119105	9.551912	9.014483
C	5.006096	8.215822	7.594762
H	5.863879	8.851613	7.41066
C	4.896634	7.004988	6.925802
H	5.666228	6.685664	6.234601
O	7.97744	2.733203	5.497303
C	4.496368	5.59151	0.600211
F	5.439893	6.321364	-0.00912
F	4.106937	4.65173	-0.26932
F	3.451143	6.386602	0.826374
C	2.951687	-1.08732	7.626869
F	1.684826	-0.87378	7.27764
F	3.295947	-2.30546	7.195905
F	2.999848	-1.1124	8.96649
O	1.845921	4.786526	4.808244
O	1.70233	2.393519	4.538014
O	-0.34	3.695467	5.088471
C	0.625104	3.923359	2.681304
S	0.939591	3.611893	4.477769
F	-0.24511	3.032076	2.235522
F	0.132147	5.140812	2.503542
F	1.745519	3.812437	1.971957
F	1.955914	3.817637	7.297378

#### Coordinates for 7a-3

Bi	3.969463	4.259301	6.543536
S	6.791579	2.561449	6.002279
O	6.72359	3.432624	7.149813
C	5.307763	4.483132	4.771317

C	6.370961	3.599852	4.630122
C	7.159983	3.610432	3.493785
H	7.993761	2.923691	3.414932
C	6.879344	4.527969	2.49093
H	7.489327	4.55843	1.597534
C	5.82125	5.410947	2.634322
C	5.023047	5.394181	3.776787
H	4.208369	6.102342	3.87767
C	4.189029	2.023497	6.522785
C	5.411918	1.468352	6.161765
C	5.570902	0.105067	5.986874
H	6.539834	-0.29357	5.712633
C	4.476017	-0.72359	6.185026
H	4.575554	-1.79407	6.05919
C	3.250201	-0.1793	6.536482
C	3.098291	1.195322	6.701884
H	2.126788	1.599609	6.964079
C	1.864888	4.512788	6.010402
C	0.93903	4.959967	6.936746
H	1.248839	5.29961	7.915748
C	-0.39615	4.992292	6.559189
H	-1.13825	5.34683	7.264365
C	-0.77902	4.581166	5.290474
H	-1.82438	4.613721	5.00738
C	0.165545	4.129502	4.380452
H	-0.13511	3.808413	3.390408
C	1.505719	4.089876	4.738978
H	2.243575	3.732919	4.027228
O	7.966985	1.809796	5.682836
C	5.542828	6.442597	1.571374
F	6.065045	7.627598	1.901751
F	6.057775	6.091472	0.389773
F	4.228683	6.620687	1.401007
C	2.070231	-1.08383	6.778282
F	0.918967	-0.48967	6.447534
F	2.159374	-2.21326	6.06938
F	1.981669	-1.42884	8.068125
S	4.05278	7.486604	7.576244
F	3.526789	9.840679	6.567047
F	5.308891	8.923979	5.76835
F	3.36665	8.217414	5.151567
O	4.726951	6.330696	6.869165
O	2.667424	7.219654	7.826173
O	4.86478	8.051449	8.597071
C	4.070674	8.697476	6.183072
F	3.948184	4.295395	8.536607

#### Coordinates for 7a-4

Bi	3.916942	4.157179	6.447265
S	6.899189	2.775792	5.762352
O	6.851381	3.74212	6.830174
C	5.059901	4.326599	4.51708
C	6.229457	3.594197	4.346314
C	6.888214	3.542879	3.130176
H	7.801155	2.967872	3.036116



C	6.364857	4.251795	2.058901	C	5.296611	5.640515	4.062685
H	6.870924	4.241992	1.101885	H	4.613215	6.467039	4.212853
C	5.194397	4.978685	2.216024	C	3.620468	2.151467	6.517883
C	4.531347	5.01127	3.439722	C	4.700358	1.421089	6.031219
H	3.612195	5.578731	3.535699	C	4.563886	0.069658	5.773061
C	4.443834	2.011192	6.67313	H	5.409613	-0.47939	5.379917
C	5.670652	1.571868	6.193802	C	3.352131	-0.55435	6.02318
C	5.982214	0.222972	6.175202	H	3.235642	-1.61092	5.819322
H	6.954452	-0.0951	5.81947	C	2.284724	0.174505	6.517667
C	5.049572	-0.68801	6.647606	C	2.40496	1.540866	6.749521
H	5.28208	-1.74542	6.657611	H	1.540667	2.104359	7.079103
C	3.827381	-0.24476	7.130422	C	2.20209	5.79392	6.968553
C	3.51102	1.110058	7.142916	C	2.442703	6.524388	8.121061
H	2.560889	1.441344	7.543854	H	3.342589	6.367058	8.700581
C	1.888365	4.510005	5.711166	C	1.488969	7.456364	8.507195
C	1.244326	5.716825	5.920082	H	1.654122	8.042103	9.403551
H	1.678414	6.480745	6.55083	C	0.337936	7.634139	7.754268
C	0.0039	5.904835	5.325641	H	-0.40134	8.3633	8.064045
H	-0.52183	6.839341	5.480345	C	0.125821	6.882695	6.608453
C	-0.56274	4.905005	4.548377	H	-0.77469	7.019541	6.021714
H	-1.53331	5.062151	4.093067	C	1.063658	5.945343	6.195766
C	0.102718	3.704222	4.350546	H	0.909885	5.356948	5.302891
H	-0.34177	2.923334	3.745255	F	4.774422	4.79545	8.122524
C	1.345872	3.498768	4.931953	O	7.166782	1.147005	5.256801
H	1.866618	2.560267	4.770396	C	6.127293	6.810291	2.011921
O	8.106805	2.099809	5.397155	F	7.116917	7.663187	2.312535
C	4.5977	5.695974	1.03404	F	6.303582	6.430901	0.74424
F	3.868003	6.748841	1.409951	F	4.9828	7.495066	2.076311
F	5.536118	6.131194	0.189748	C	0.989661	-0.5246	6.836495
F	3.788915	4.880453	0.340817	F	-0.05518	0.297968	6.74305
C	2.81337	-1.24821	7.614746	F	0.772605	-1.56133	6.025796
F	2.113063	-1.74809	6.584625	F	1.009194	-1.00328	8.090272
F	3.39907	-2.27794	8.230852	O	2.431772	4.079944	4.472924
F	1.940998	-0.70515	8.462207	S	2.3266	3.004328	3.439959
S	2.537186	4.626182	9.532162	O	3.548247	2.266619	3.289185
F	0.233464	3.841483	10.49817	O	1.096268	2.282938	3.528741
F	0.718058	2.997731	8.570016	C	2.187791	4.038713	1.91852
F	1.701483	2.267673	10.34454	F	2.040955	3.267162	0.852772
O	3.46459	3.845401	8.633221	F	1.14326	4.855715	2.005592
O	3.095855	4.839178	10.82237	F	3.283779	4.779267	1.756486
O	1.898038	5.702383	8.835904				
C	1.217602	3.356263	9.760202				
F	4.622076	5.875703	7.143737				

#### Coordinates for **7a-trans-2**

Bi	3.754019	4.336164	6.42662
S	6.315839	2.138697	5.842675
O	6.623882	2.745084	7.105005
C	5.330415	4.568053	4.92964
C	6.159581	3.479904	4.682399
C	6.971581	3.468683	3.561495
H	7.602646	2.608983	3.376312
C	6.957325	4.551772	2.696921
H	7.581119	4.545169	1.812136
C	6.128686	5.632561	2.950226

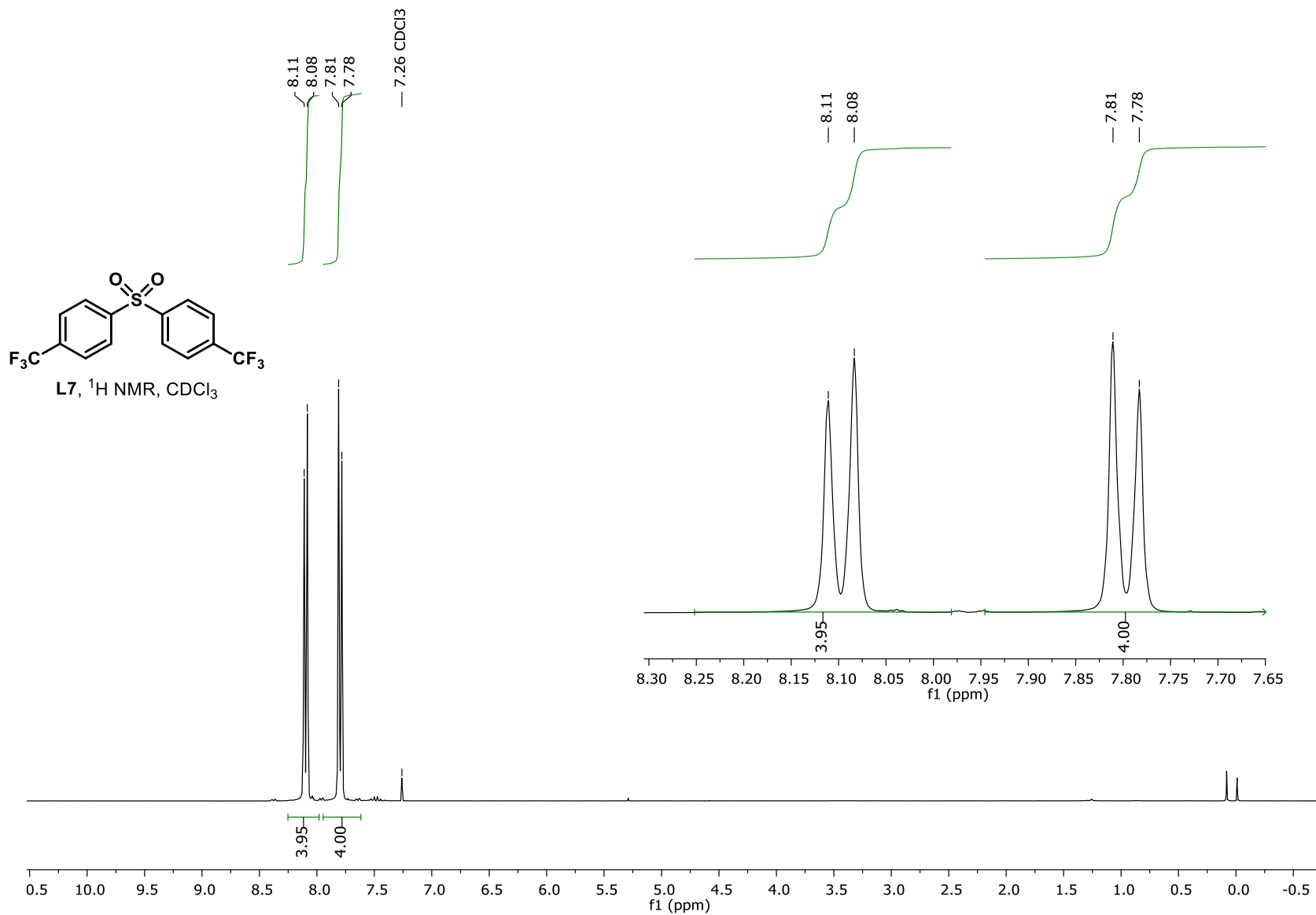
## 7. References

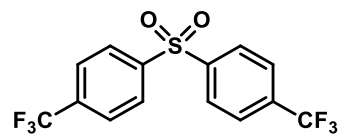
1. Fulmer, G. R.; Miller, A. J. M.; Sherden, N. H.; Gottlieb, H. E.; Nudelman, A.; Stoltz, B. M.; Bercaw, J. E.; Goldberg, K. I. NMR Chemical Shifts of Trace Impurities: Common Laboratory Solvents, Organics, and Gases in Deuterated Solvents Relevant to the Organometallic Chemist. *Organometallics* **2010**, *29*, 2176-2179.
2. Gopalsamy, A.; Shi, M.; Stauffer, B.; Bahat, R.; Billiard, J.; Ponce-de-Leon, H.; Seestaller-Wehr, L.; Fukayama, S.; Mangine, A.; Moran, R.; Krishnamurthy, G.; Bodine, P. Identification of Diarylsulfone Sulfonamides as Secreted Frizzled Related Protein-1 (sFRP-1) Inhibitors. *J. Med. Chem.* **2008**, *51*, 7670-7672.
3. Lamers, P.; Priebbenow, D. L.; Bolm, C. Iron-Catalyzed Acylative Dealkylation of N-Alkylsulfoximines. *Eur. J. Org. Chem.* **2015**, *2015*, 5594-5602.
4. Teng, F.; Cheng, J.; Bolm, C. Silver-Mediated N-Trifluoromethylation of Sulfoximines. *Org. Lett.* **2015**, *17*, 3166-3169.
5. Okauchi, T.; Kuramoto, K.; Kitamura, M., Facile Preparation of Aryl Sulfides Using Palladium Catalysis under Mild Conditions. *Synlett* **2010**, *2010*, 2891-2894.
6. Dyer, J. C.; Harris, D. L.; Evans, S. A. Oxygen-17 nuclear magnetic resonance spectroscopy of sulfoxides and sulfones. Alkyl substituent-induced chemical-shift effects. *J. Org. Chem.* **1982**, *47*, 3660-3664.
7. Chen, H.-Y.; Peng, W.-T.; Lee, Y.-H.; Chang, Y.-L.; Chen, Y.-J.; Lai, Y.-C.; Jheng, N.-Y.; Chen, H.-Y. Use of Base Control To Provide High Selectivity between Diaryl Thioether and Diaryl Disulfide for C–S Coupling Reactions of Aryl Halides and Sulfur and a Mechanistic Study. *Organometallics* **2013**, *32*, 5514-5522.
8. Planas, O.; Wang, F.; Leutzsch, M.; Cornella, J. Fluorination of arylboronic esters enabled by bismuth redox catalysis. *Science* **2020**, *367*, 313.
9. Worrell, B. T.; Ellery, S. P.; Fokin, V. V. Copper(I)-Catalyzed Cycloaddition of Bismuth(III) Acetylides with Organic Azides: Synthesis of Stable Triazole Anion Equivalents. *Angew. Chem. Int. Ed.* **2013**, *52*, 13037-13041.
10. Jurrat, M.; Maggi, L.; Lewis, W.; Ball, L. T., Modular bismacrocycles for the selective C–H arylation of phenols and naphthols. *Nat. Chem.* **2020**, *12*, 260-269.
11. Si, T.; Li, B.; Xiong, W.; Xu, B.; Tang, W. Efficient cross-coupling of aryl/alkenyl triflates with acyclic secondary alkylboronic acids. *Org. Biomol. Chem.* **2017**, *15*, 9903-9909.
12. Gill, D.; Hester, A. J.; Lloyd-Jones, G. C. On the preparation of ortho-trifluoromethyl phenyl triflate. *Org. Biomol. Chem.* **2004**, *2*, 2547-2548.

13. Goossen, L. J.; Rodríguez, N.; Linder, C. Decarboxylative Biaryl Synthesis from Aromatic Carboxylates and Aryl Triflates. *J. Am. Chem. Soc.* **2008**, *130*, 15248-15249.
14. Goossen, L. J.; Linder, C.; Rodríguez, N.; Lange, P. P. Biaryl and Aryl Ketone Synthesis via Pd-Catalyzed Decarboxylative Coupling of Carboxylate Salts with Aryl Triflates. *Chem. Eur. J.* **2009**, *15*, 9336-9349.
15. He, R.-D.; Li, C.-L.; Pan, Q.-Q.; Guo, P.; Liu, X.-Y.; Shu, X.-Z. Reductive Coupling between C–N and C–O Electrophiles. *J. Am. Chem. Soc.* **2019**, *141*, 12481-12486.
16. Mills, L. R.; Graham, J. M.; Patel, P.; Rousseaux, S. A. L. Ni-Catalyzed Reductive Cyanation of Aryl Halides and Phenol Derivatives via Transnitration. *J. Am. Chem. Soc.* **2019**, *141*, 19257-19262.
17. Yang, S.; Chen, M.; Tang, P. Visible-Light Photoredox-Catalyzed and Copper-Promoted Trifluoromethoxylation of Arenediazonium Tetrafluoroborates. *Angew. Chem. Int. Ed.* **2019**, *58*, 7840-7844.
18. Greenhalgh, M. D.; Kolodziej, A.; Sinclair, F. Thomas, S. P., Iron-Catalyzed Hydromagnesiation: Synthesis and Characterization of Benzylic Grignard Reagent Intermediate and Application in the Synthesis of Ibuprofen. *Organometallics* **2014**, *33*, 5811-5819.
19. Green, A. E.; Agouridas, V.; Deniau, E. Cesium carbonate mediated aryl triflate esters' deprotection. *Tetrahedron Lett.* **2013**, *54*, 7078-7079.
20. Harper, M. J.; Emmett, E. J.; Bower, J. F.; Russell, C. A. Oxidative 1,2-Difunctionalization of Ethylene via Gold-Catalyzed Oxyarylation. *J. Am. Chem. Soc.* **2017**, *139*, 12386-12389.
21. Reeves, E. K.; Humke, J. N.; Neufeldt, S. R., N-Heterocyclic Carbene Ligand-Controlled Chemodivergent Suzuki–Miyaura Cross Coupling. *J. Org. Chem.* **2019**, *84*, 11799-11812.
22. Finke, A. D.; Elleby, E. C.; Boyd, M. J.; Weissman, H.; Moore, J. S. Zinc Chloride-Promoted Aryl Bromide–Alkyne Cross-Coupling Reactions at Room Temperature. *J. Org. Chem.* **2009**, *74* (22), 8897-8900.
23. Scheidt, F.; Neufeld, J.; Schäfer, M.; Thiehoff, C.; Gilmour, R. Catalytic Geminal Difluorination of Styrenes for the Construction of Fluorine-rich Bioisosteres. *Org. Lett.* **2018**, *20*, 8073-8076.
24. Uemura, M.; Yorimitsu, H.; Oshima, K. Cp\*Li as a base: application to palladium-catalyzed cross-coupling reaction of aryl-X or alkenyl-X (X=I, Br, OTf, ONf) with terminal acetylenes. *Tetrahedron* **2008**, *64*, 1829-1833.
25. Anderson, K. W.; Mendez-Perez, M.; Priego, J.; Buchwald, S. L. Palladium-Catalyzed Amination of Aryl Nonaflates. *J. Org. Chem.* **2003**, *68*, 9563-9573.
26. Neese, F. The ORCA program system. *WIREs Comp. Mol. Sci.* **2012**, *2*, 73-78.

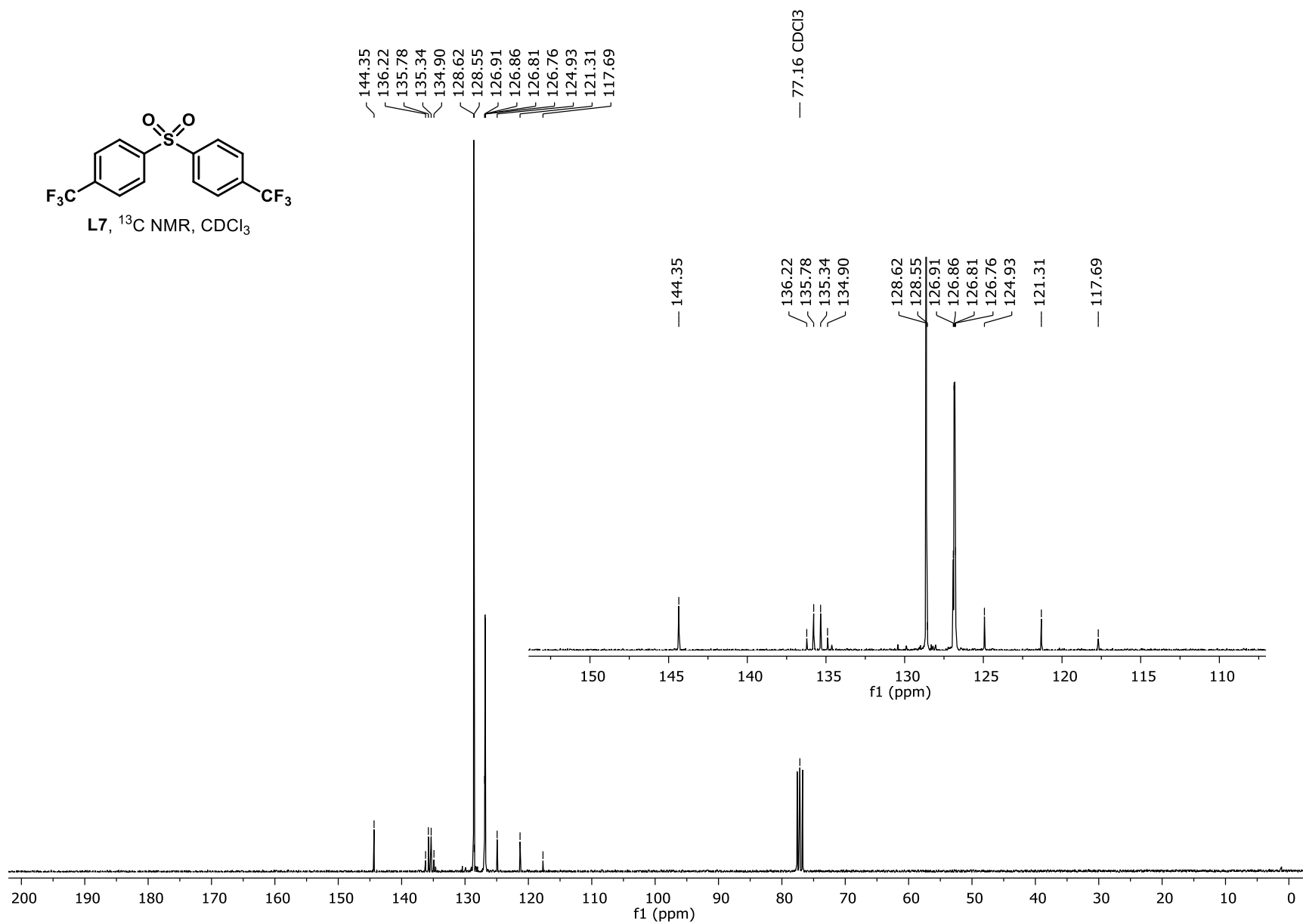
27. Neese, F. Software update: the ORCA program system, version 4.0. *WIREs Comp. Mol. Sci.* **2018**, 8, e1327.
28. Adamo, C.; Barone, V. Toward reliable density functional methods without adjustable parameters: The PBE0 model. *J. Chem. Phys.* **1999**, 110, 6158-6170.
29. Perdew, J. P.; Ernzerhof, M.; Burke, K. Rationale for mixing exact exchange with density functional approximations. *J. Chem. Phys.* **1996**, 105, 9982-9985.
30. Weigend, F.; Ahlrichs, R. Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, 7, 3297-3305.
31. Weigend, F., Accurate Coulomb-fitting basis sets for H to Rn. *Phys. Chem. Chem. Phys.* **2006**, 8, 1057-1065.
32. Metz, B.; Stoll, H.; Dolg, M. Small-core multiconfiguration-Dirac-Hartree-Fock-adjusted pseudopotentials for post-d main group elements: Application to PbH and PbO. *J. Chem. Phys.* **2000**, 113, 2563-2569.
33. Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, 132, 154104.
34. Becke, A. D.; Johnson, E. R. A density-functional model of the dispersion interaction. *J. Chem. Phys.* **2005**, 123, 154101.
35. Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, approximate and parallel Hartree-Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree-Fock exchange. *Chem. Phys.* **2009**, 356, 98-109.
36. Reed, A. E.; Curtiss, L. A.; Weinhold, F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chem. Rev.* **1988**, 88, 899-926.
37. *Chemcraft Version 1.8, h. w. c. c. .*
38. Muetterties, E. L.; Mahler, W.; Schmutzler, R. Stereochemistry of Phosphorus(V) Fluorides. *Inorg. Chem.* **1963**, 2, 613-618.

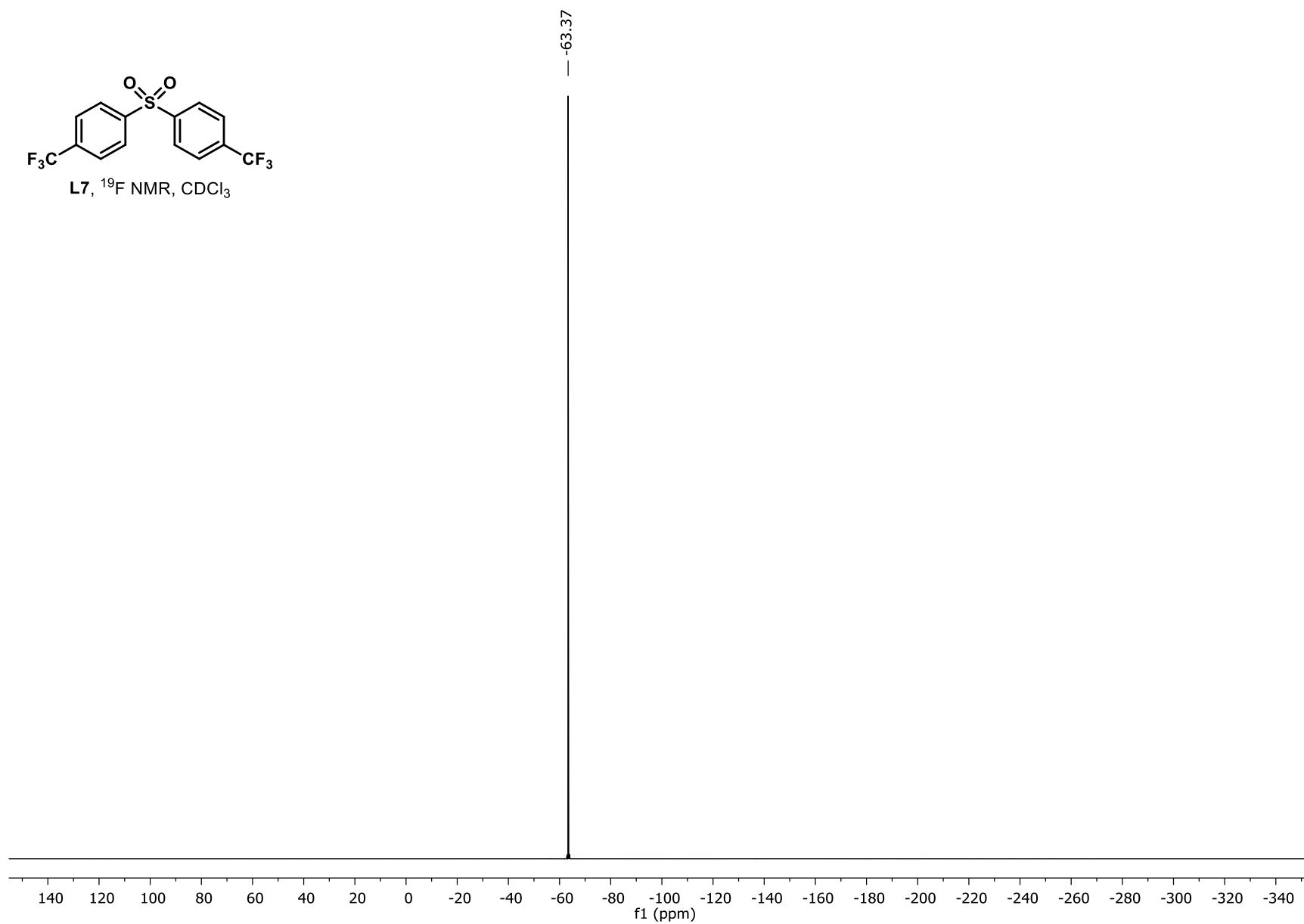
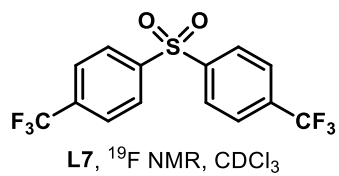
## 8. NMR characterization of L7



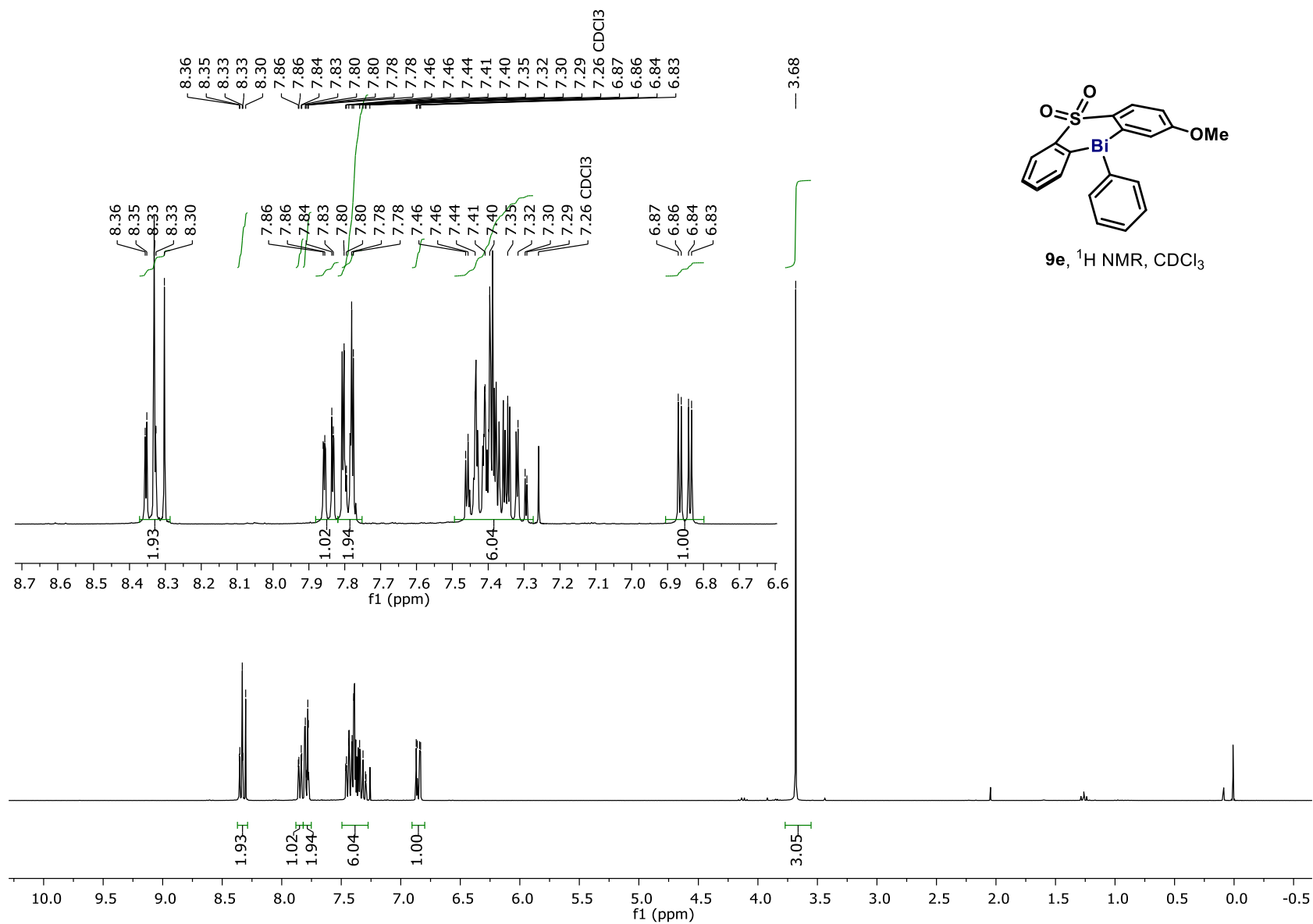


L7,  $^{13}\text{C}$  NMR,  $\text{CDCl}_3$

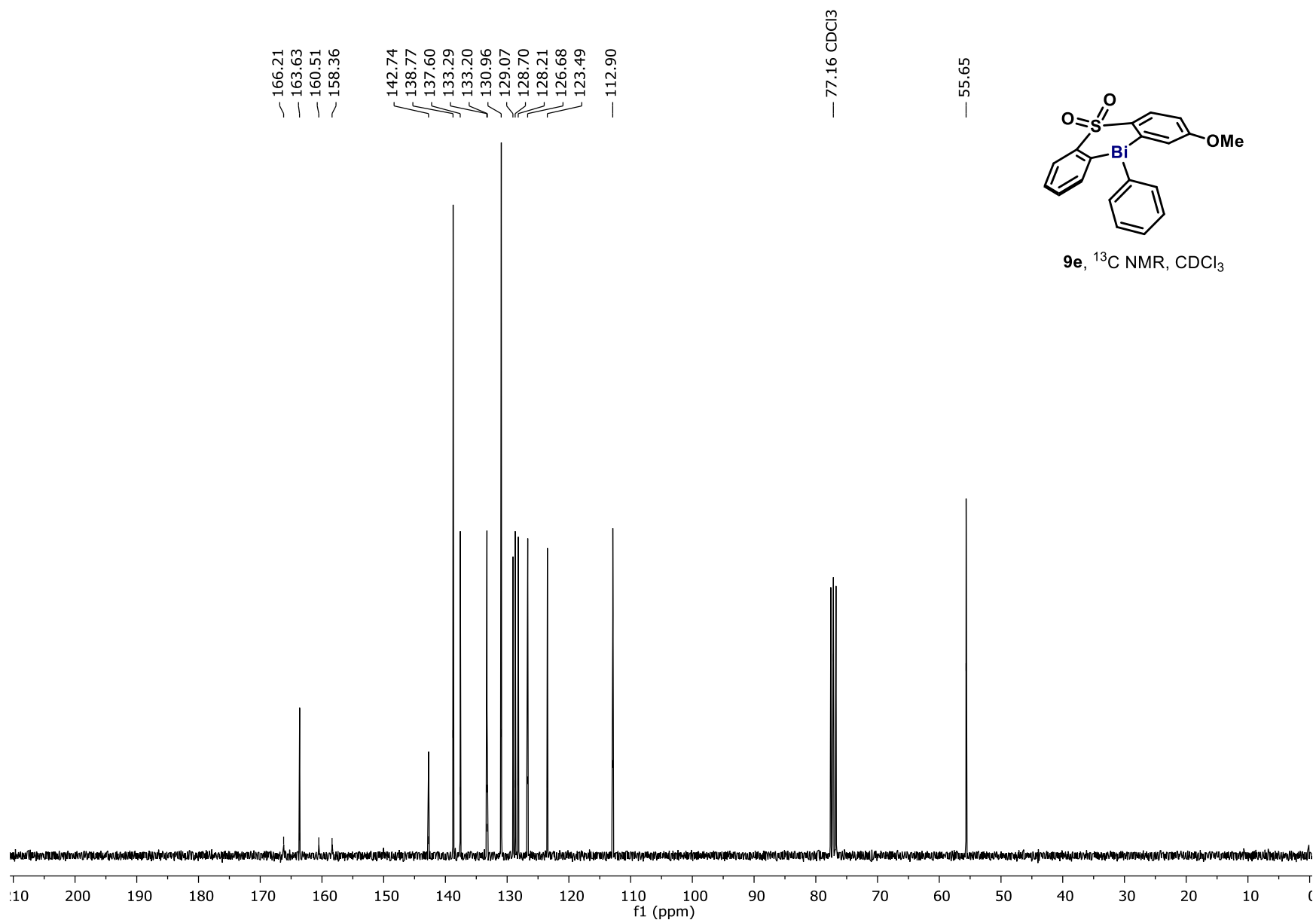


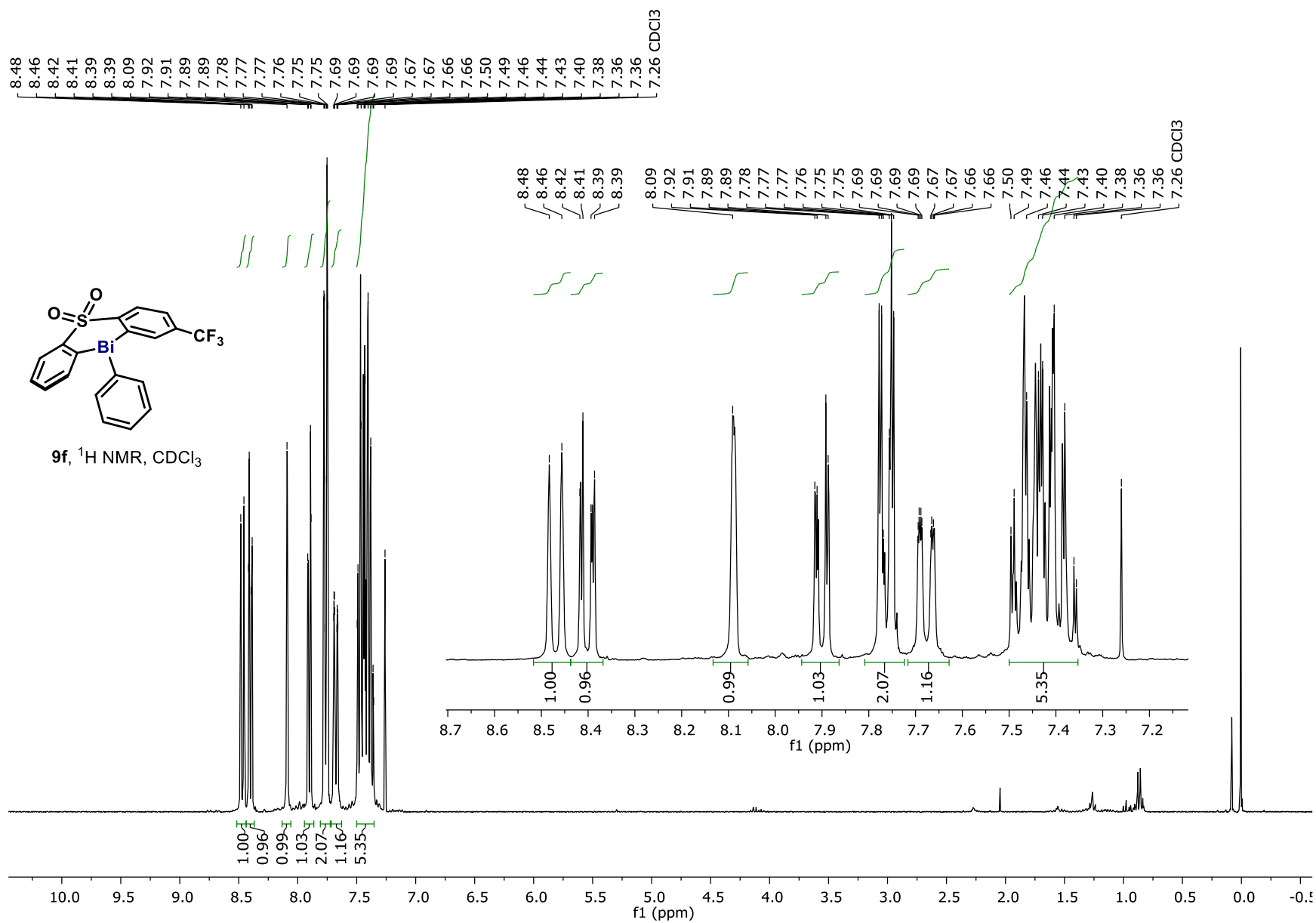


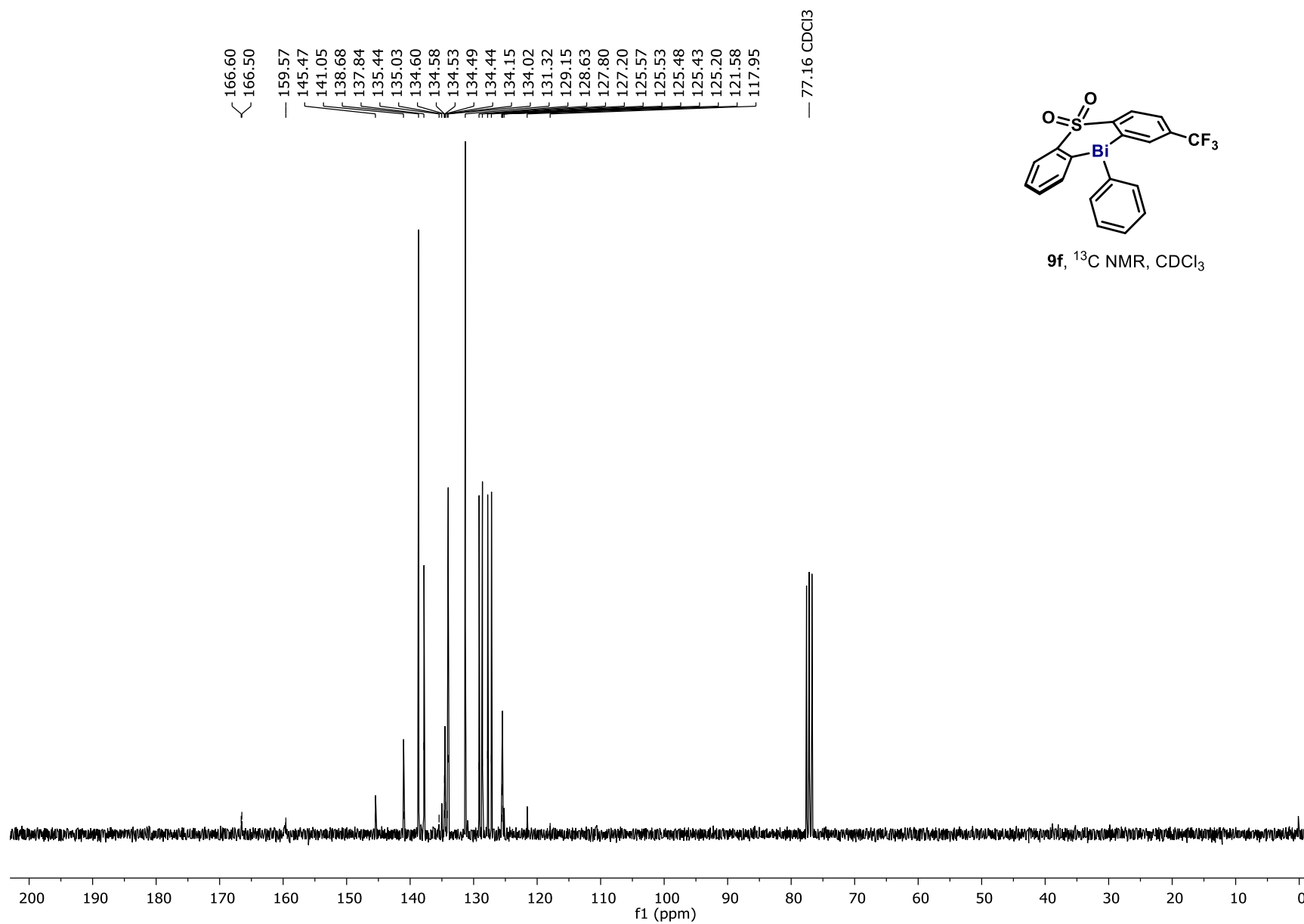
## 9. NMR characterization of Bi(III) compounds

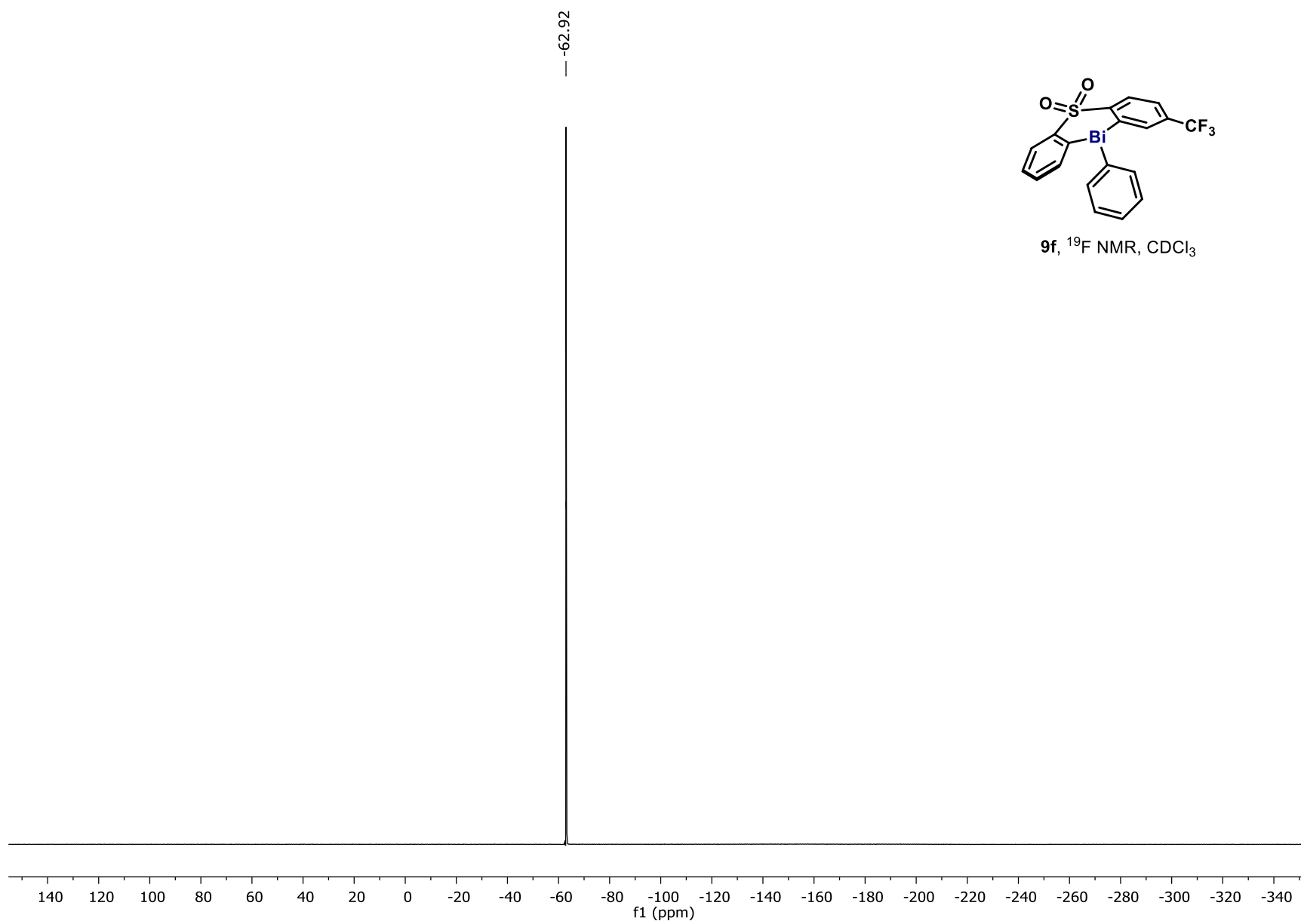


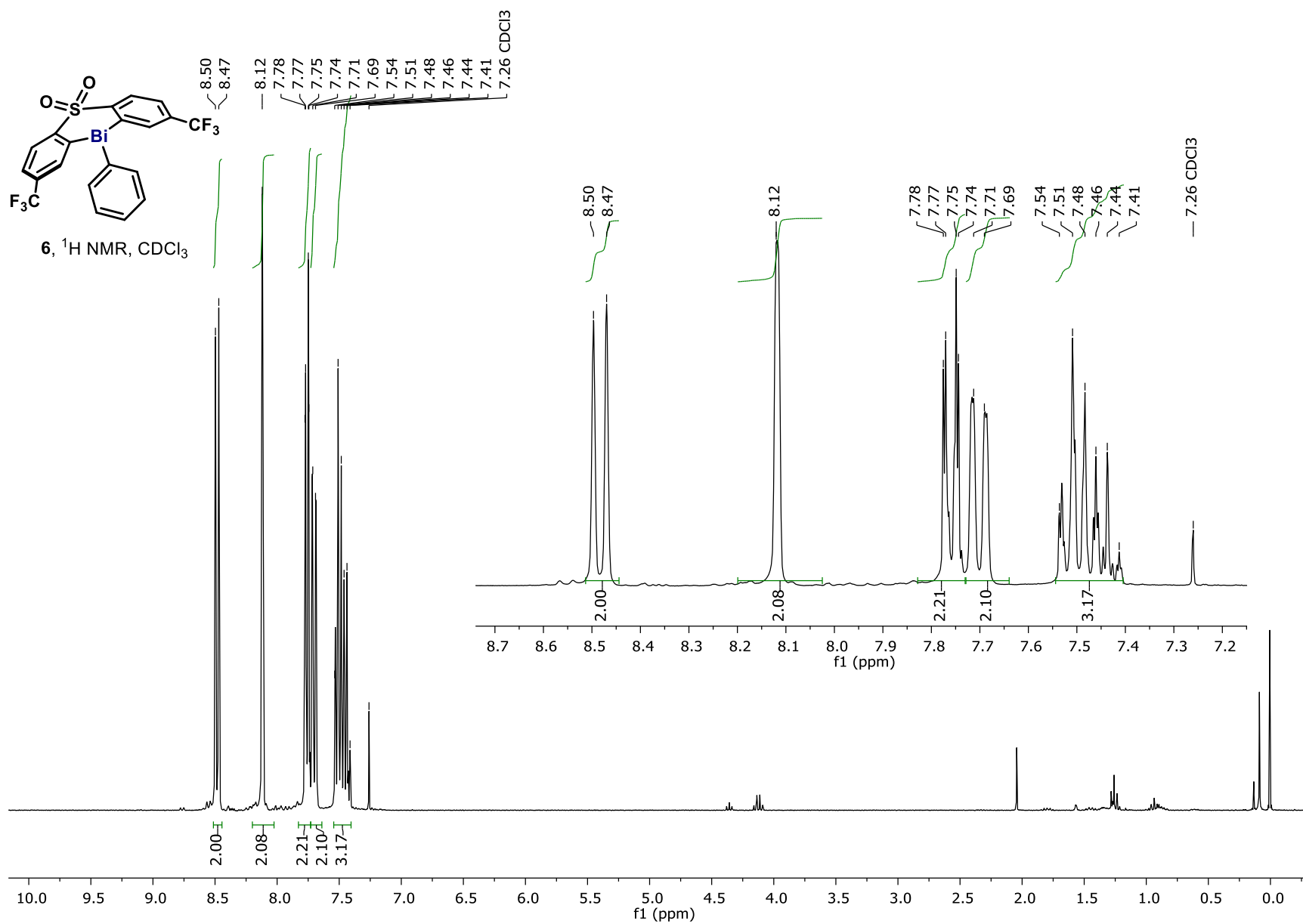


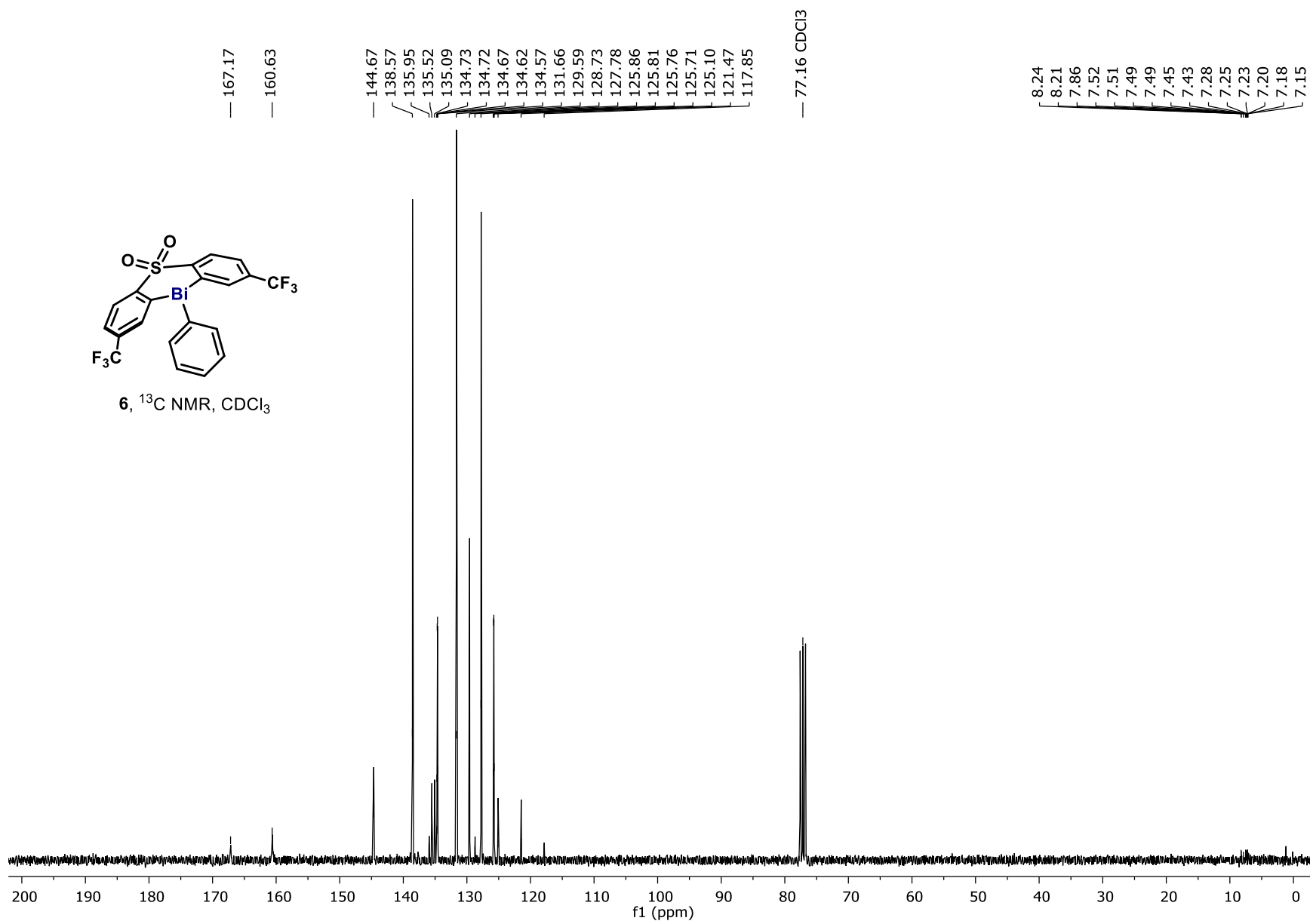


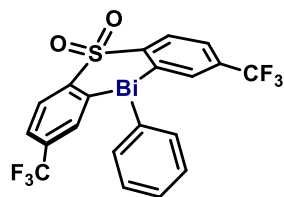




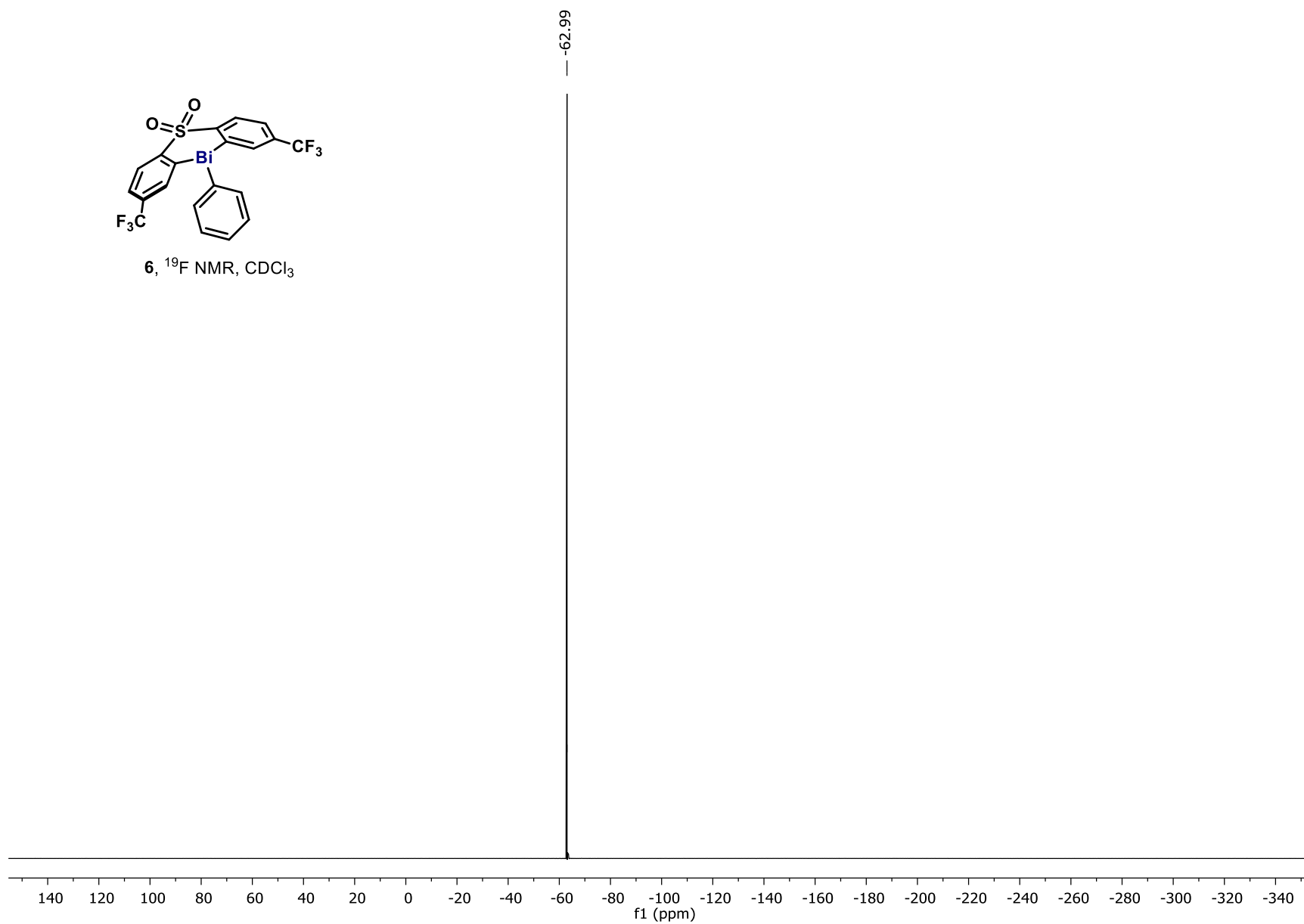


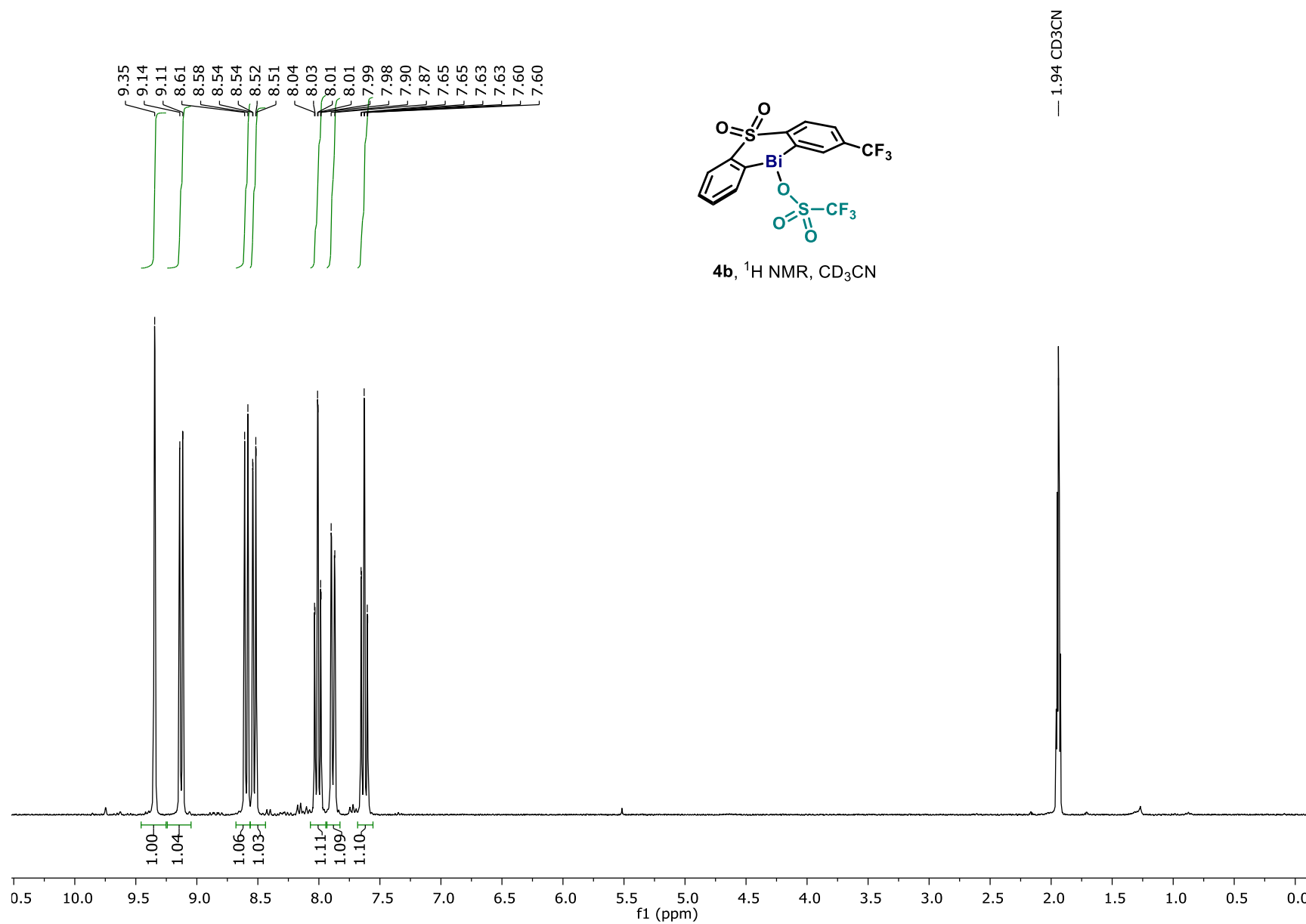




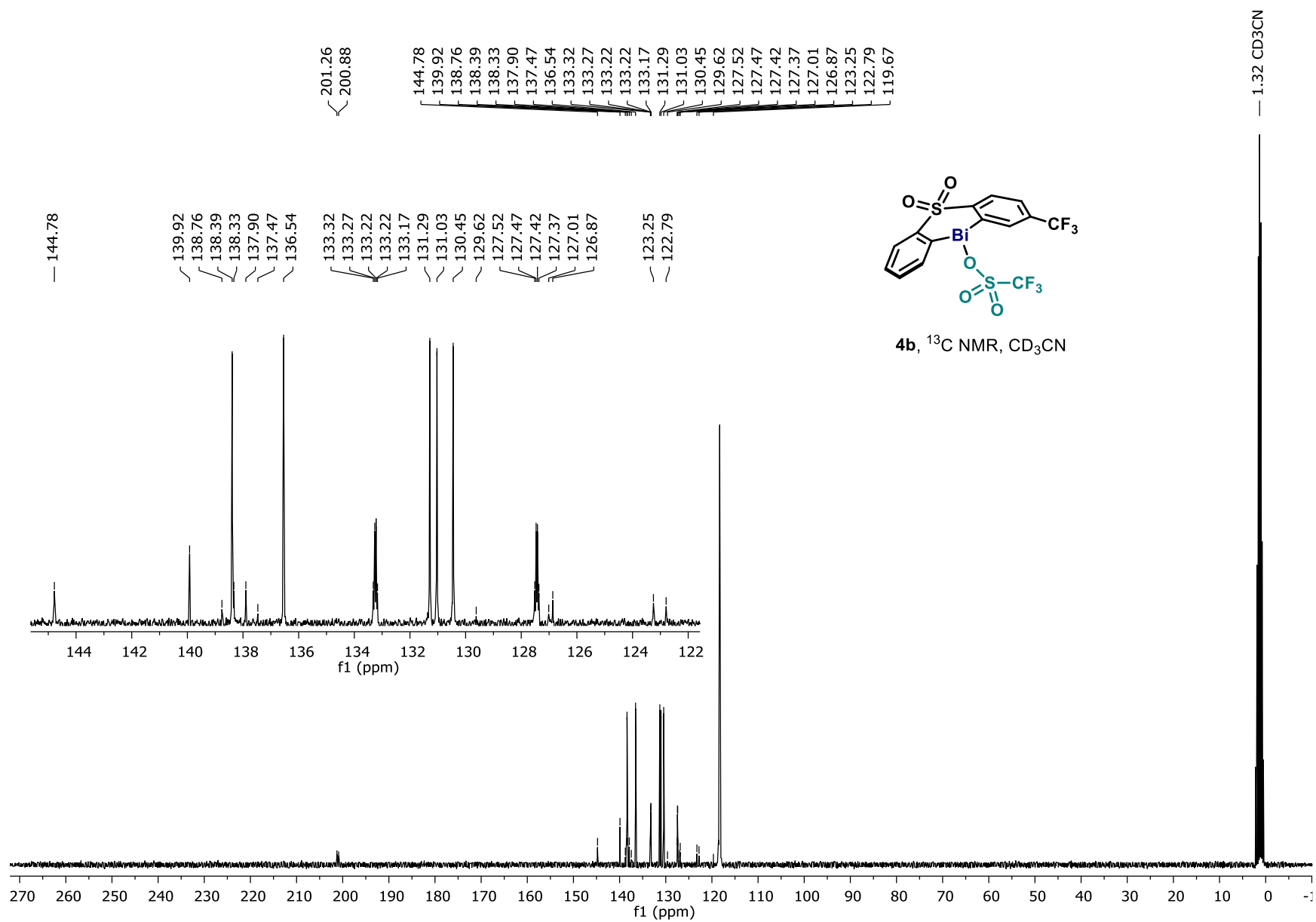


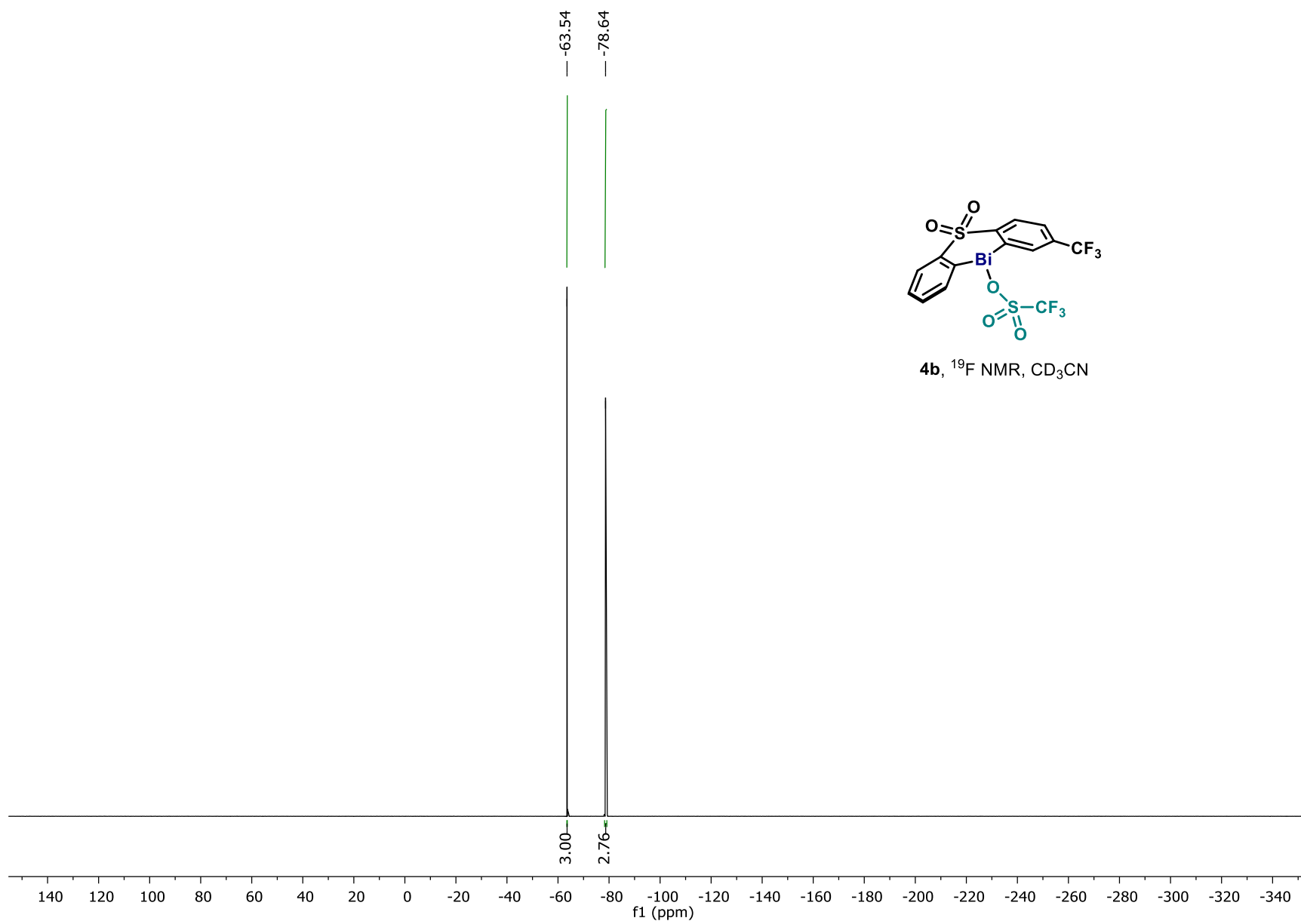
6,  $^{19}\text{F}$  NMR,  $\text{CDCl}_3$

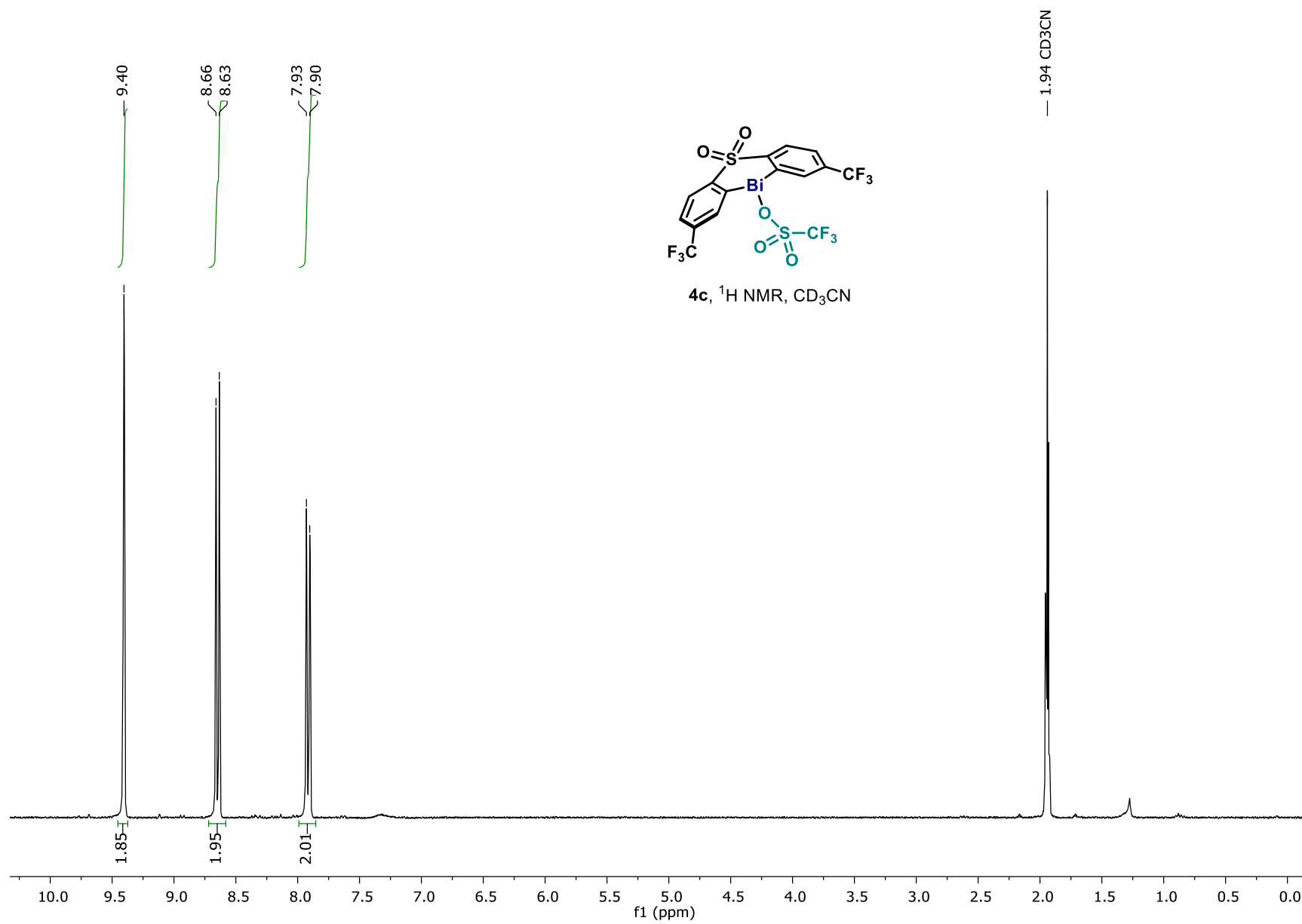


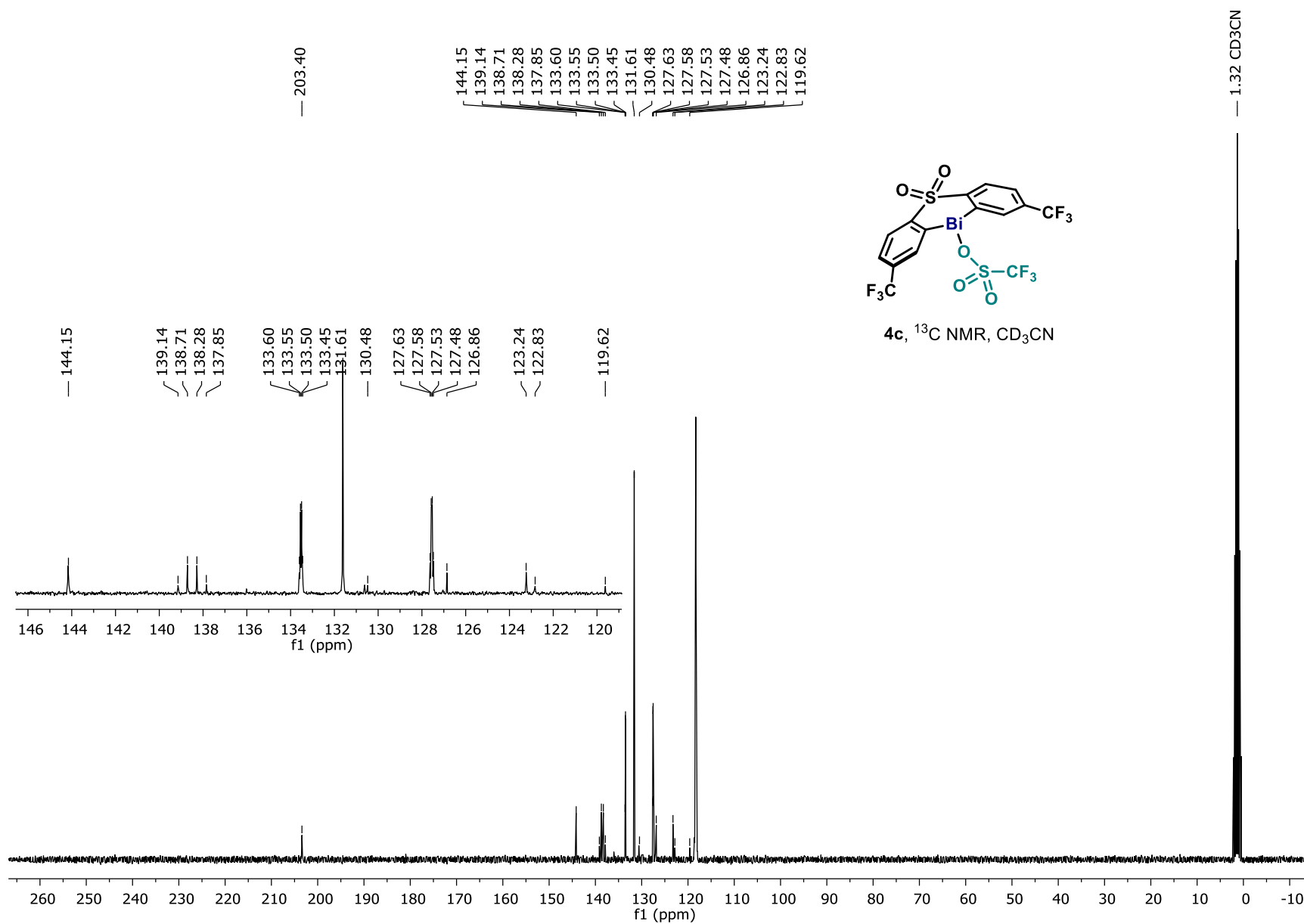


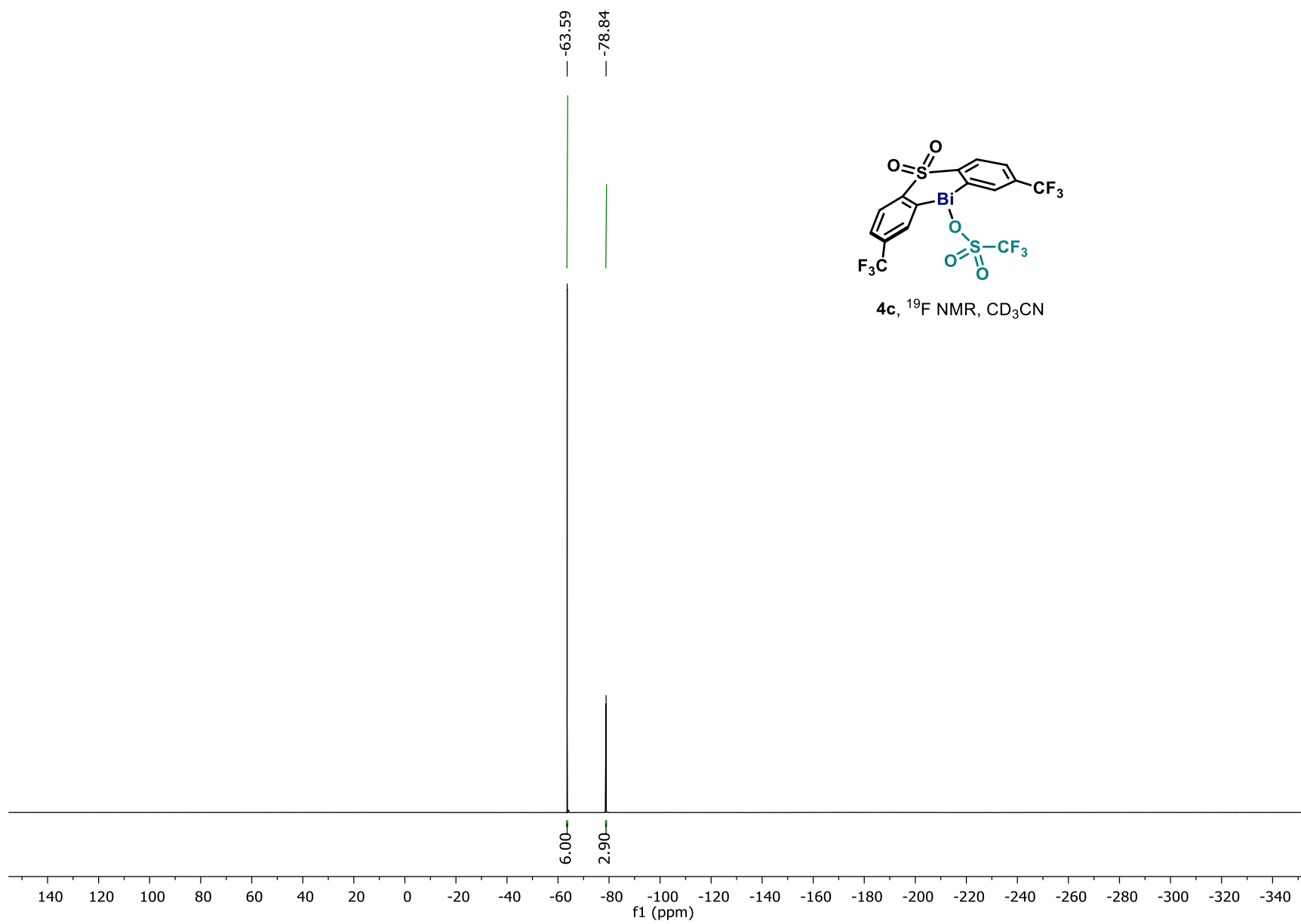




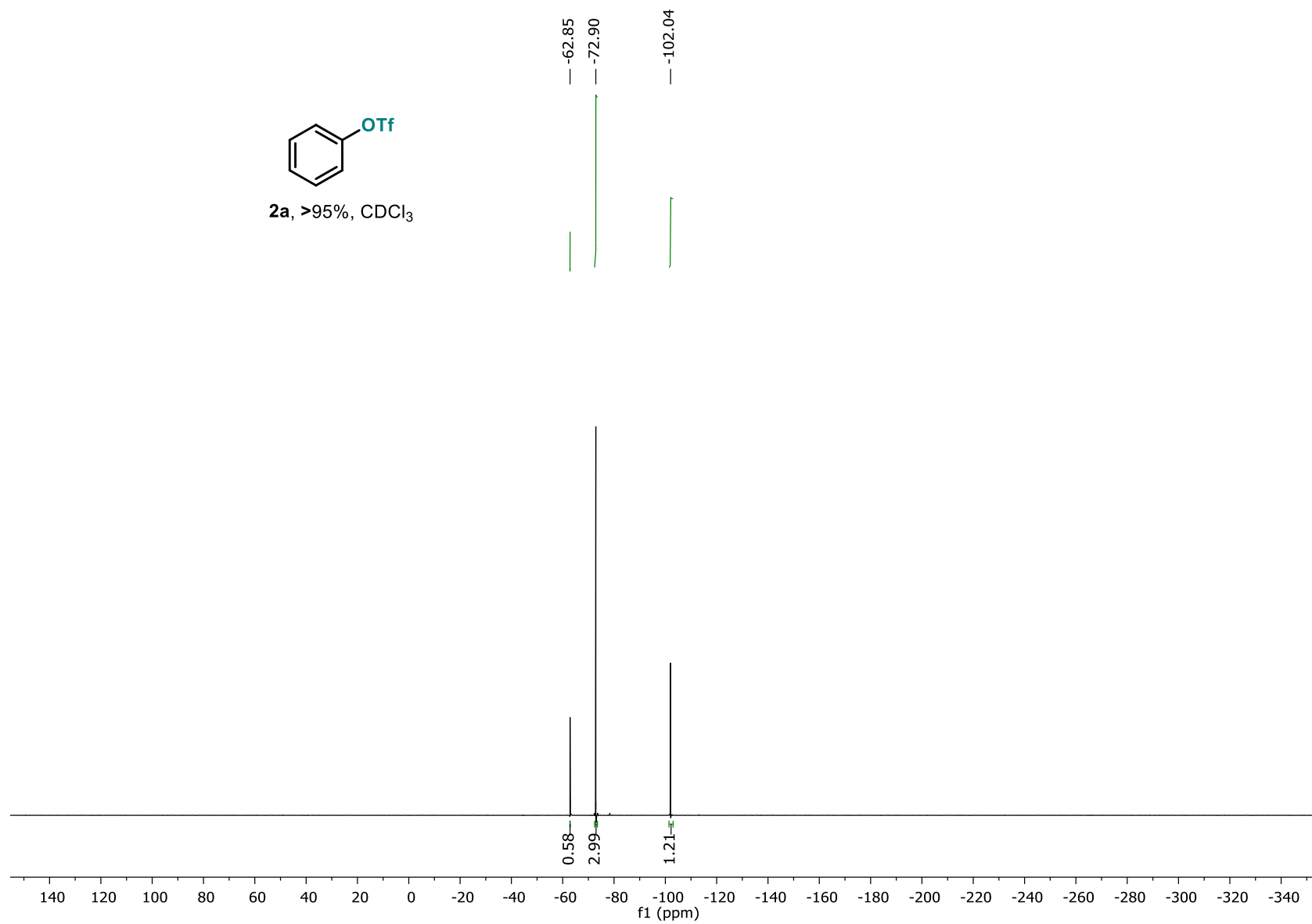
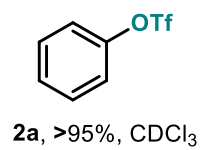


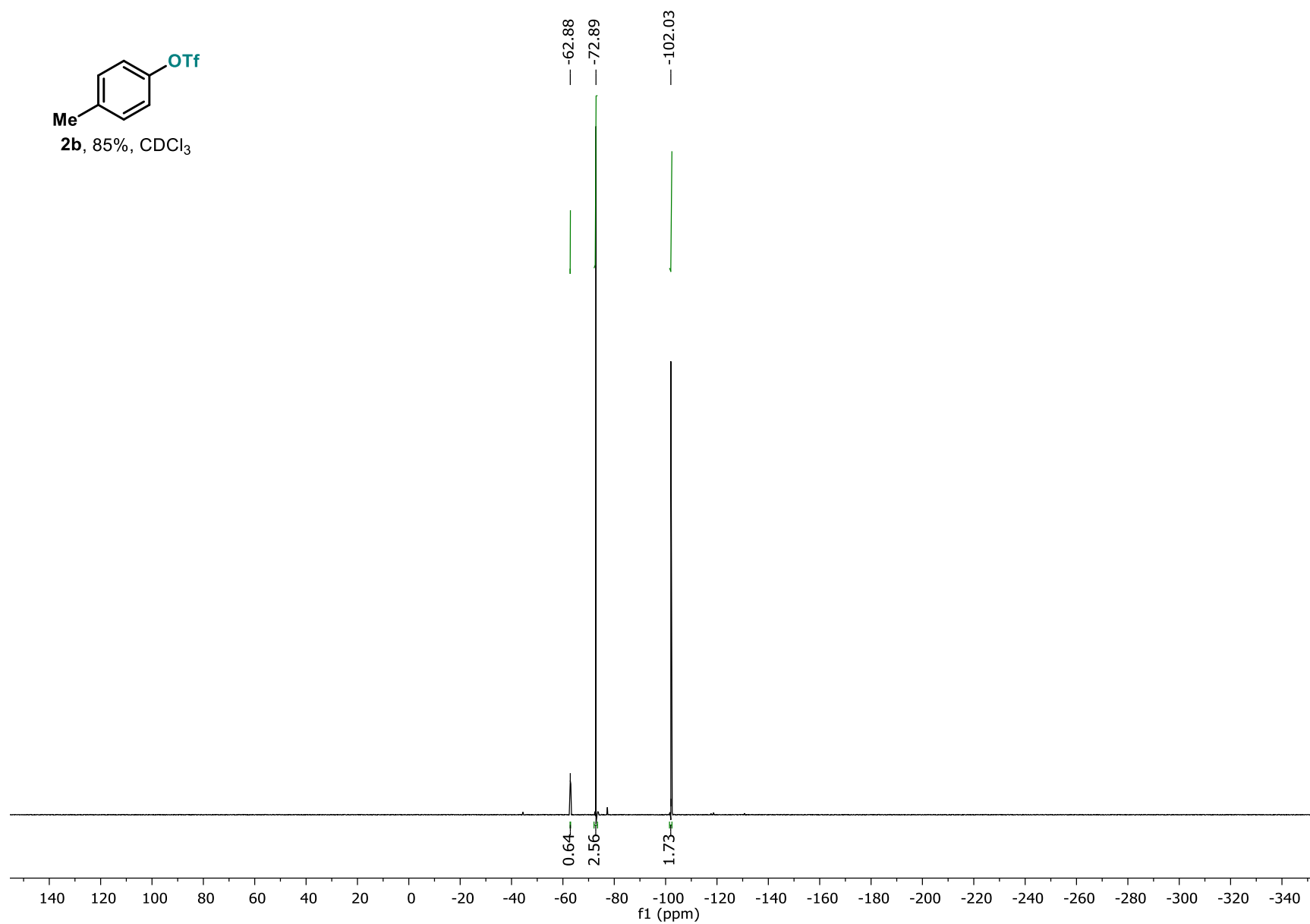
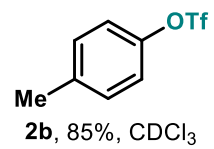


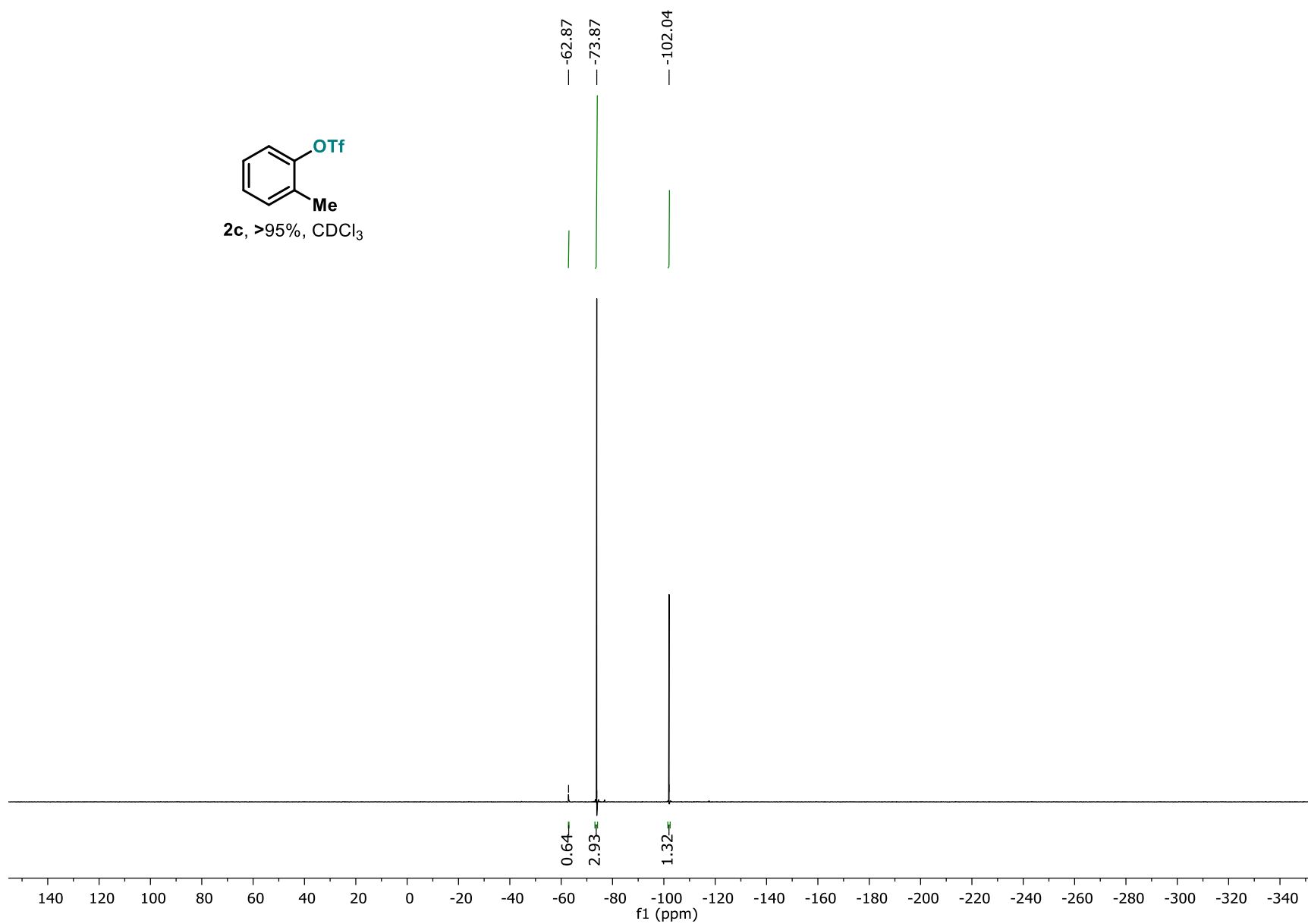
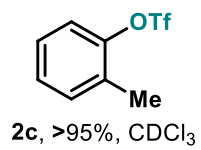




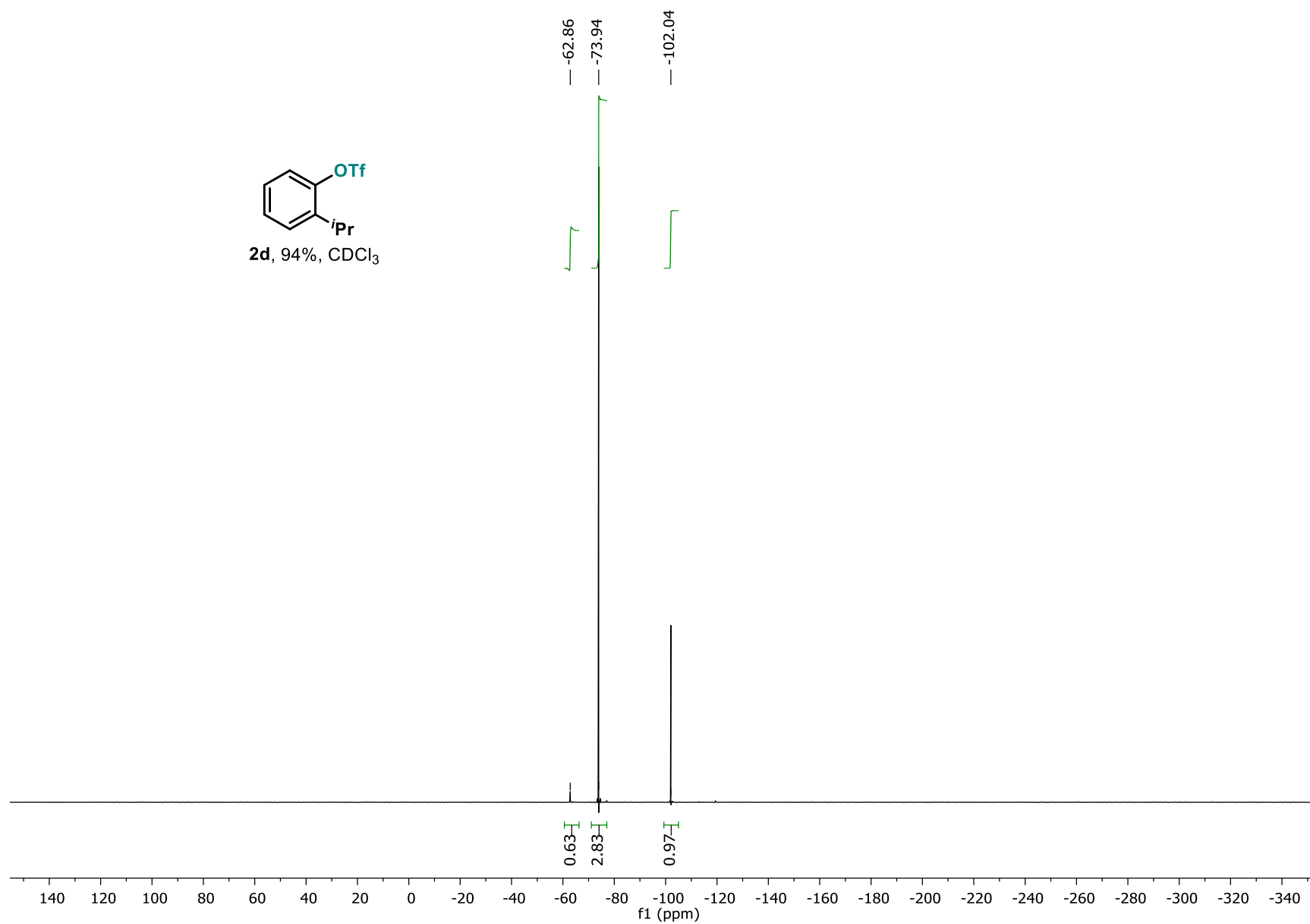
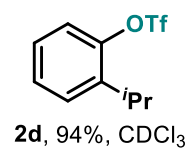
10.  $^{19}\text{F}$  NMR yields of the Bi-catalyzed coupling of arylboronic acids with NaOTf

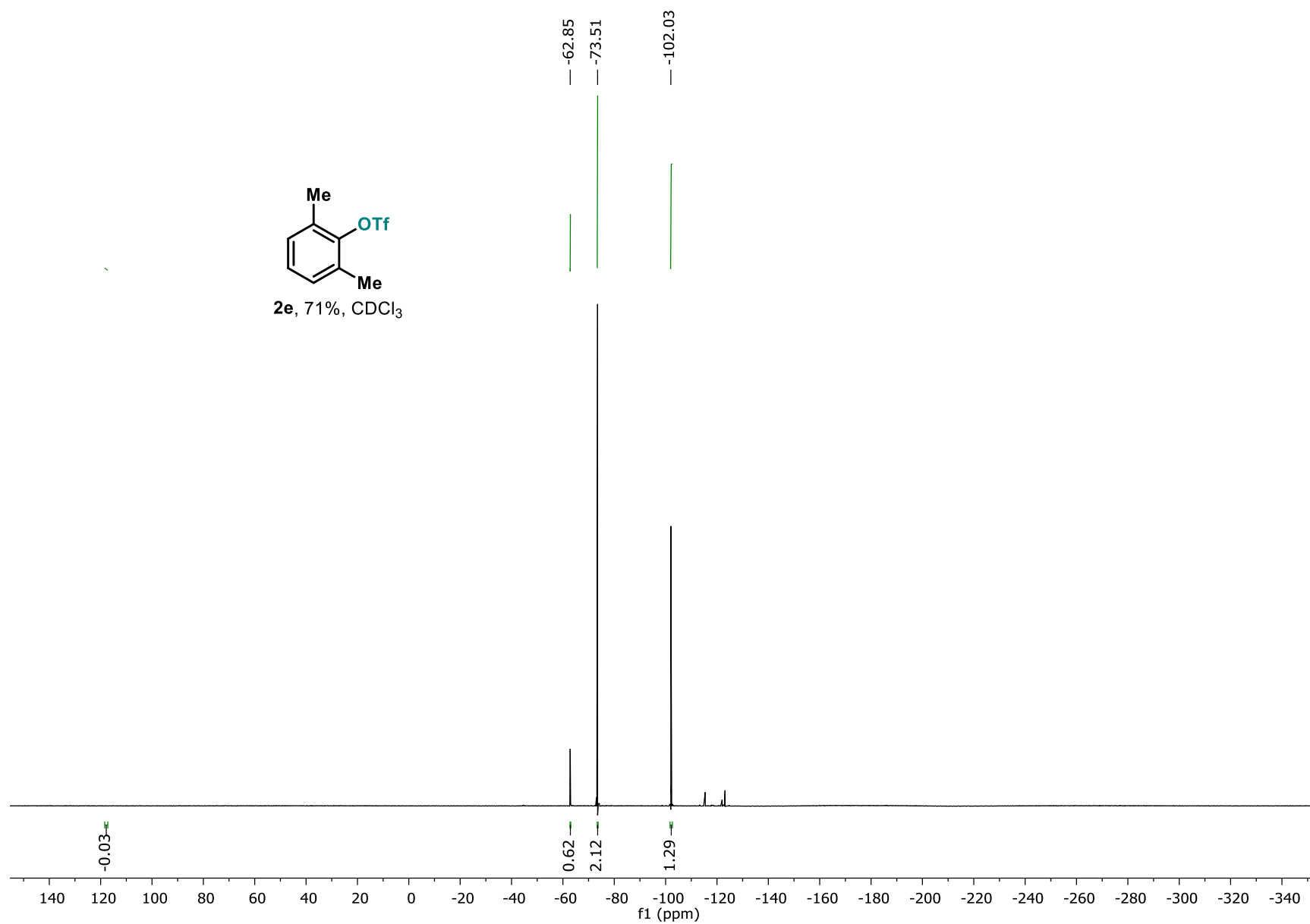
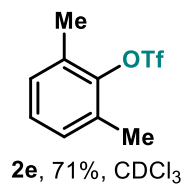


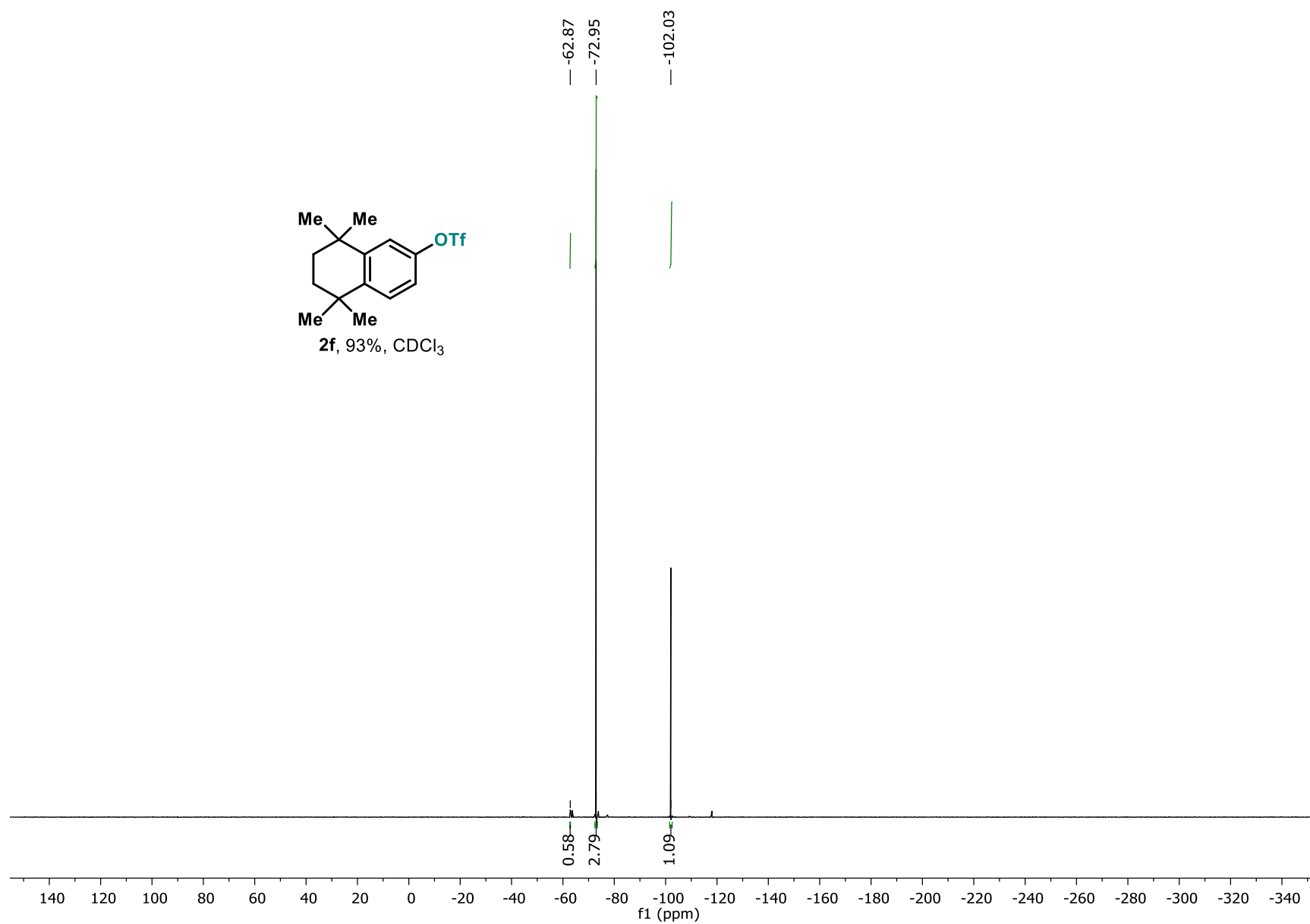
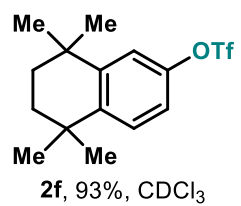


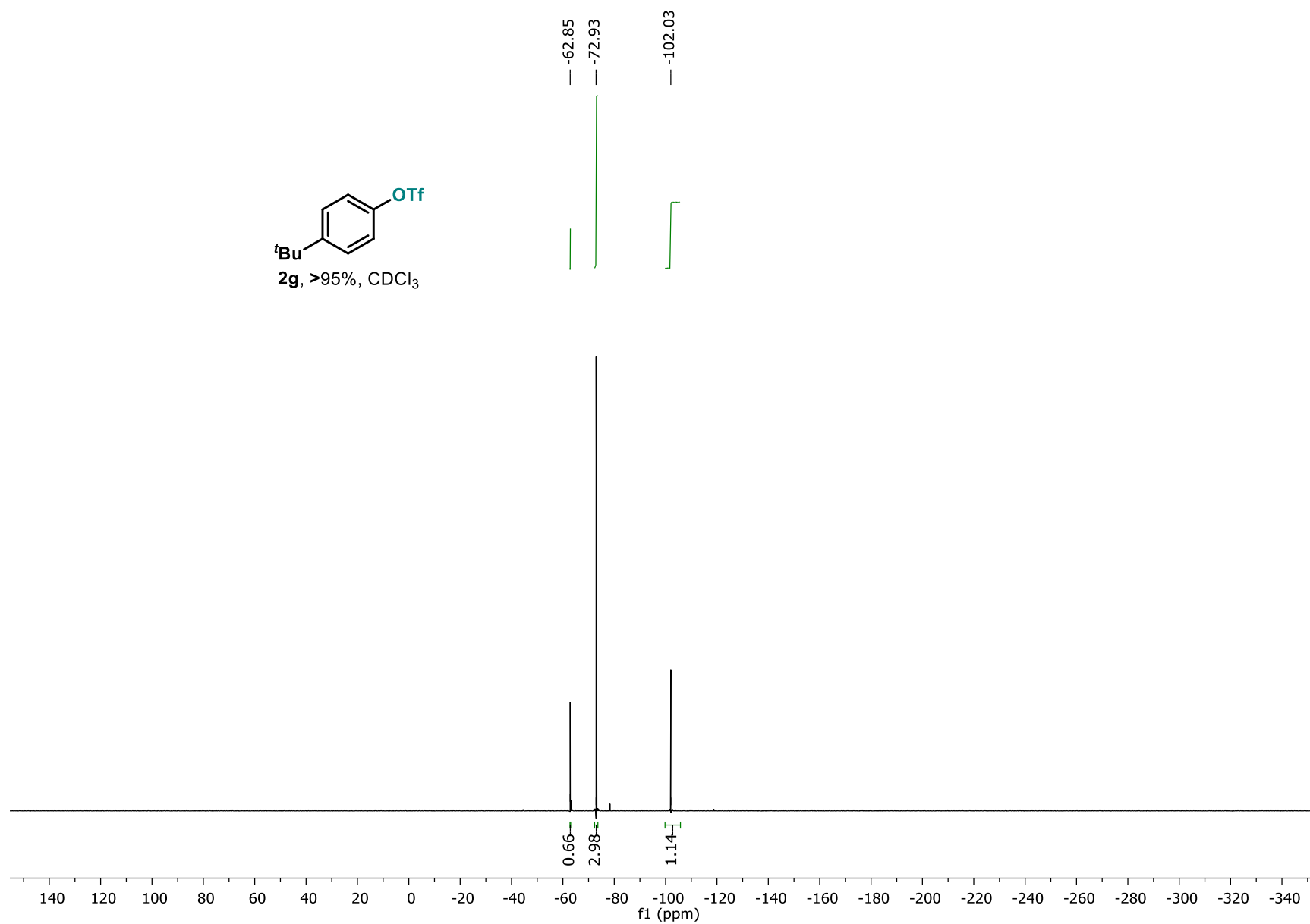
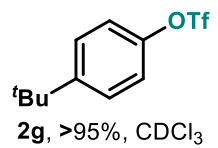


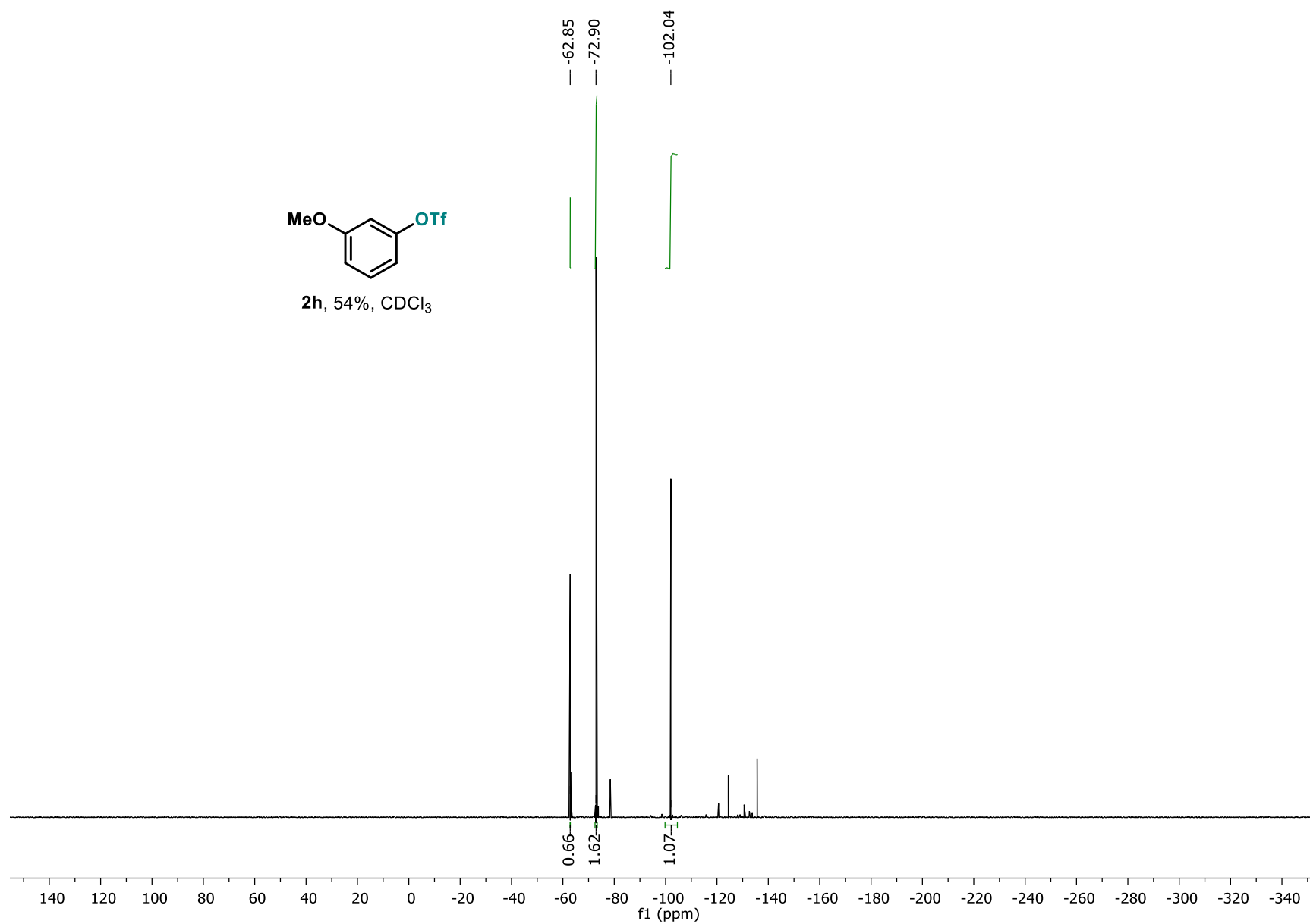
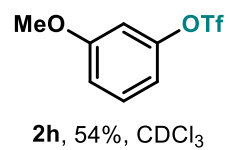


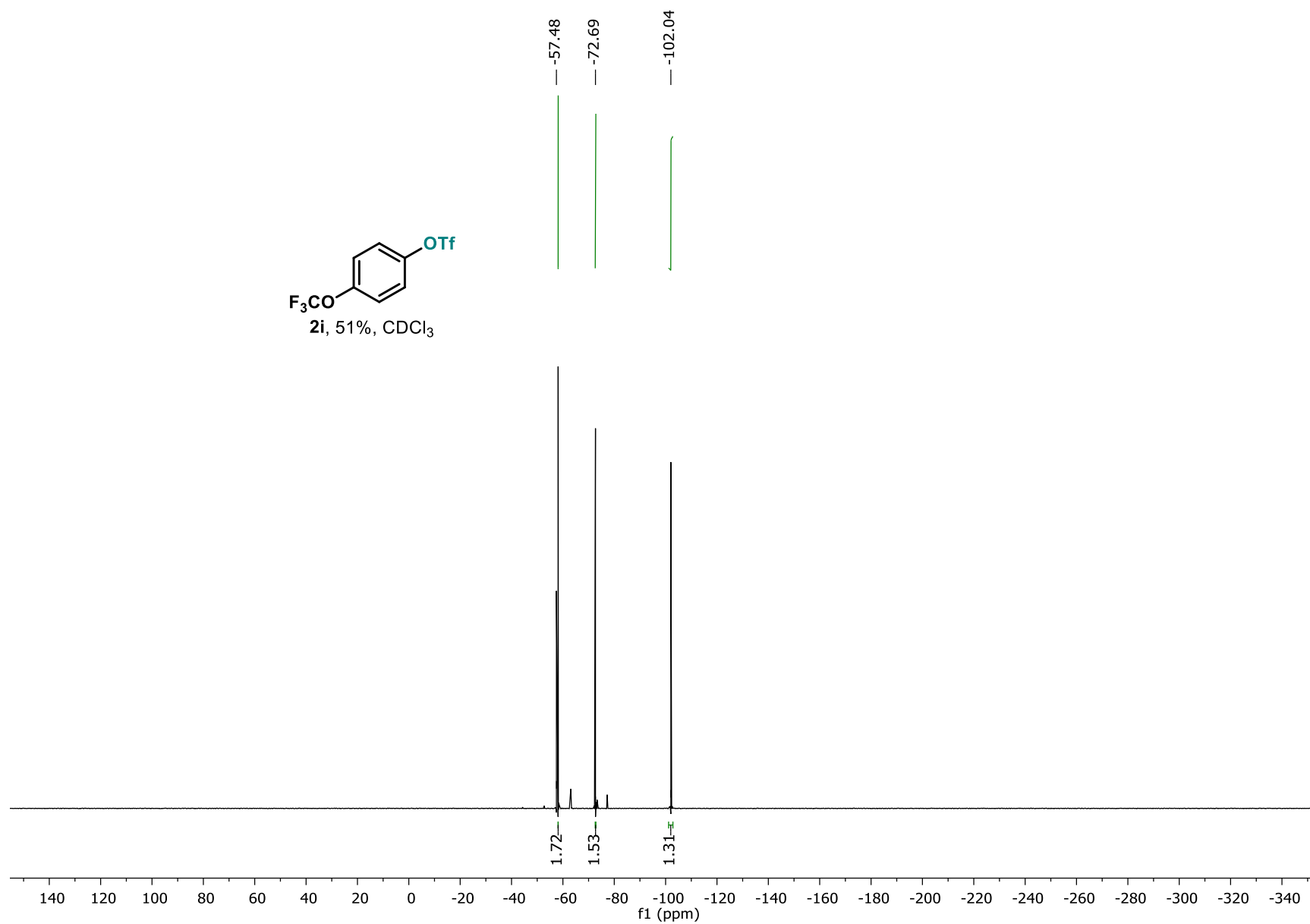
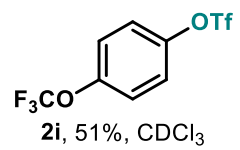


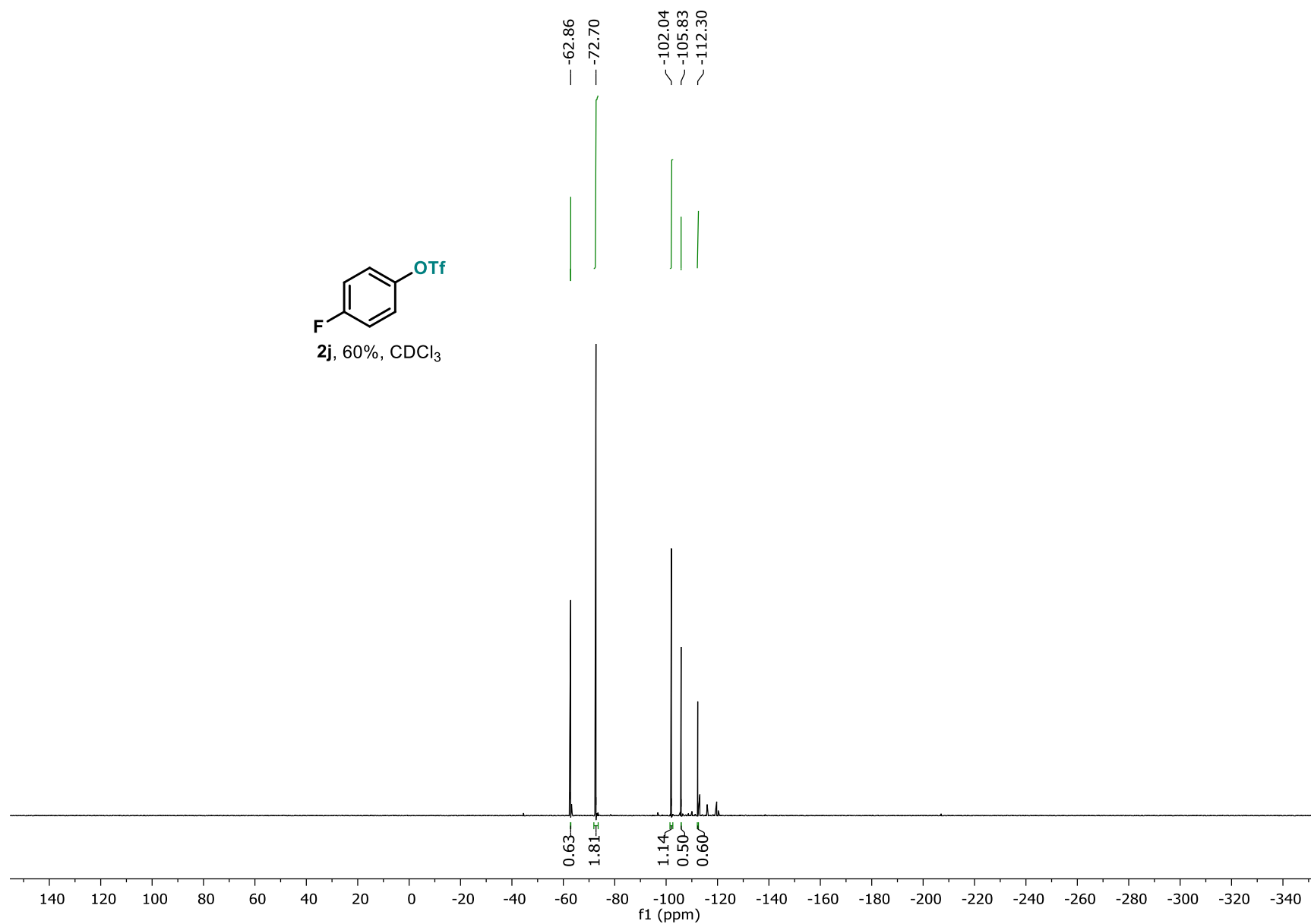
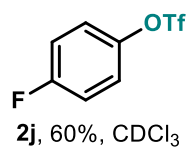


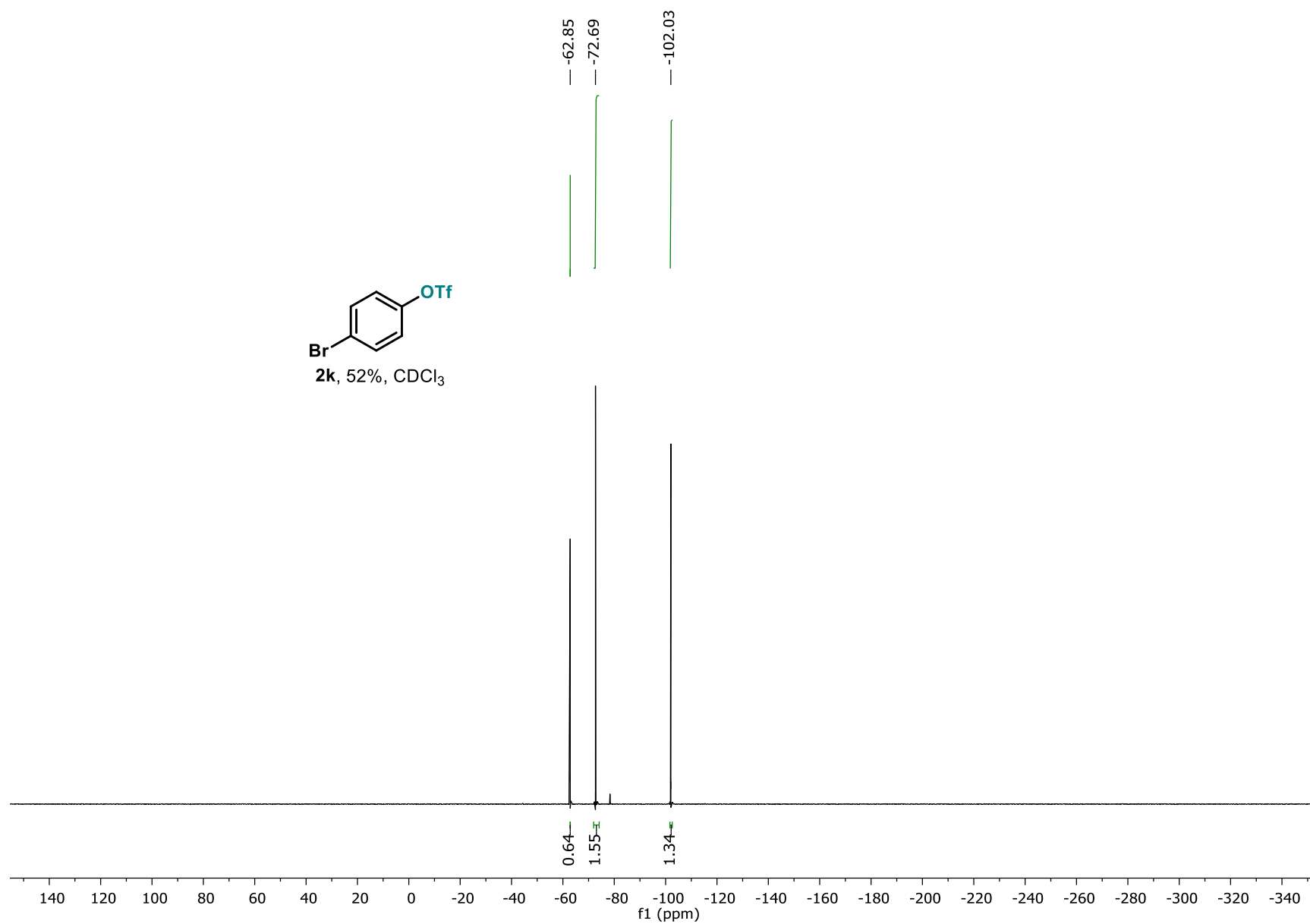
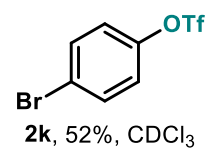




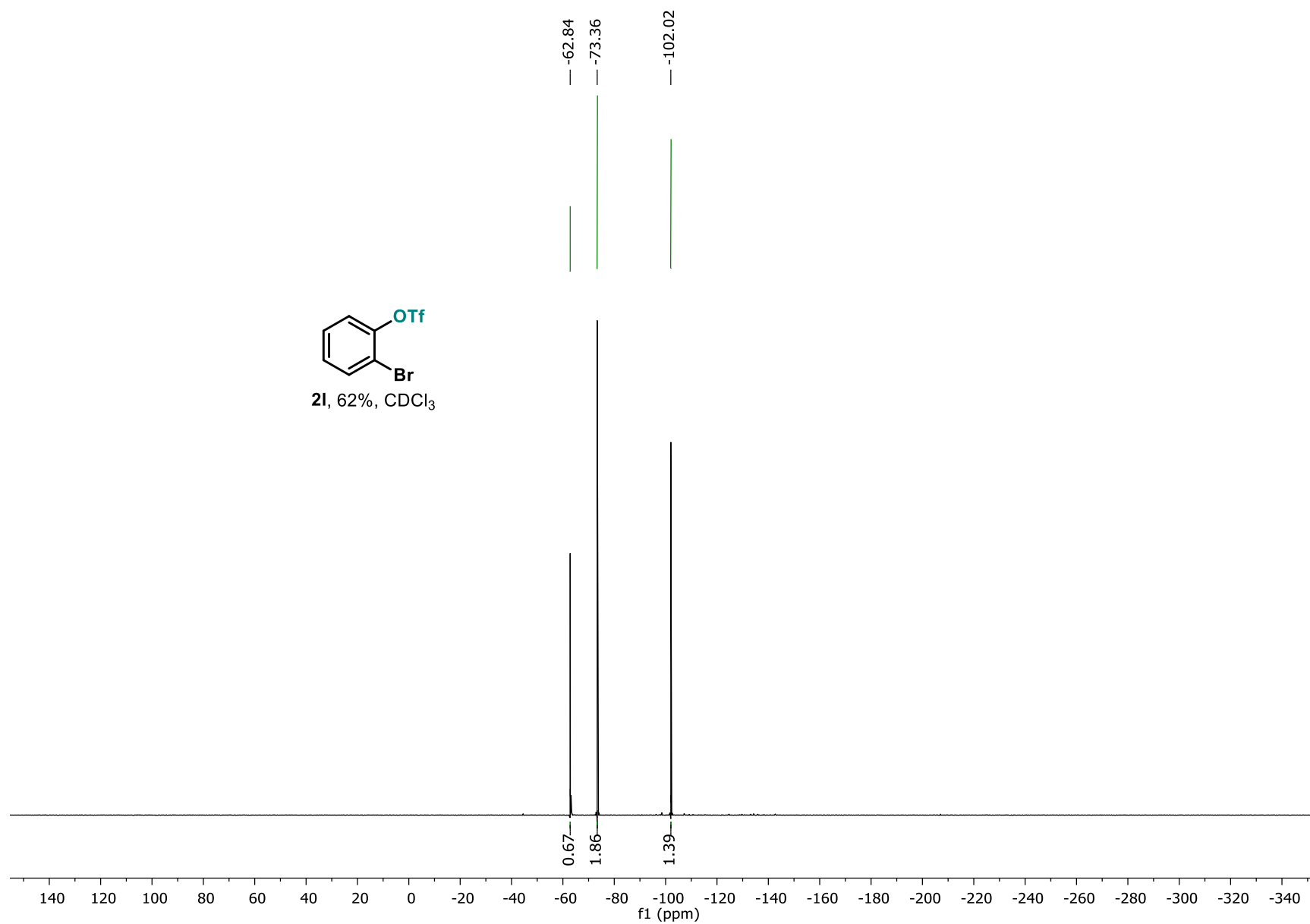
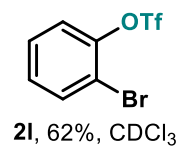


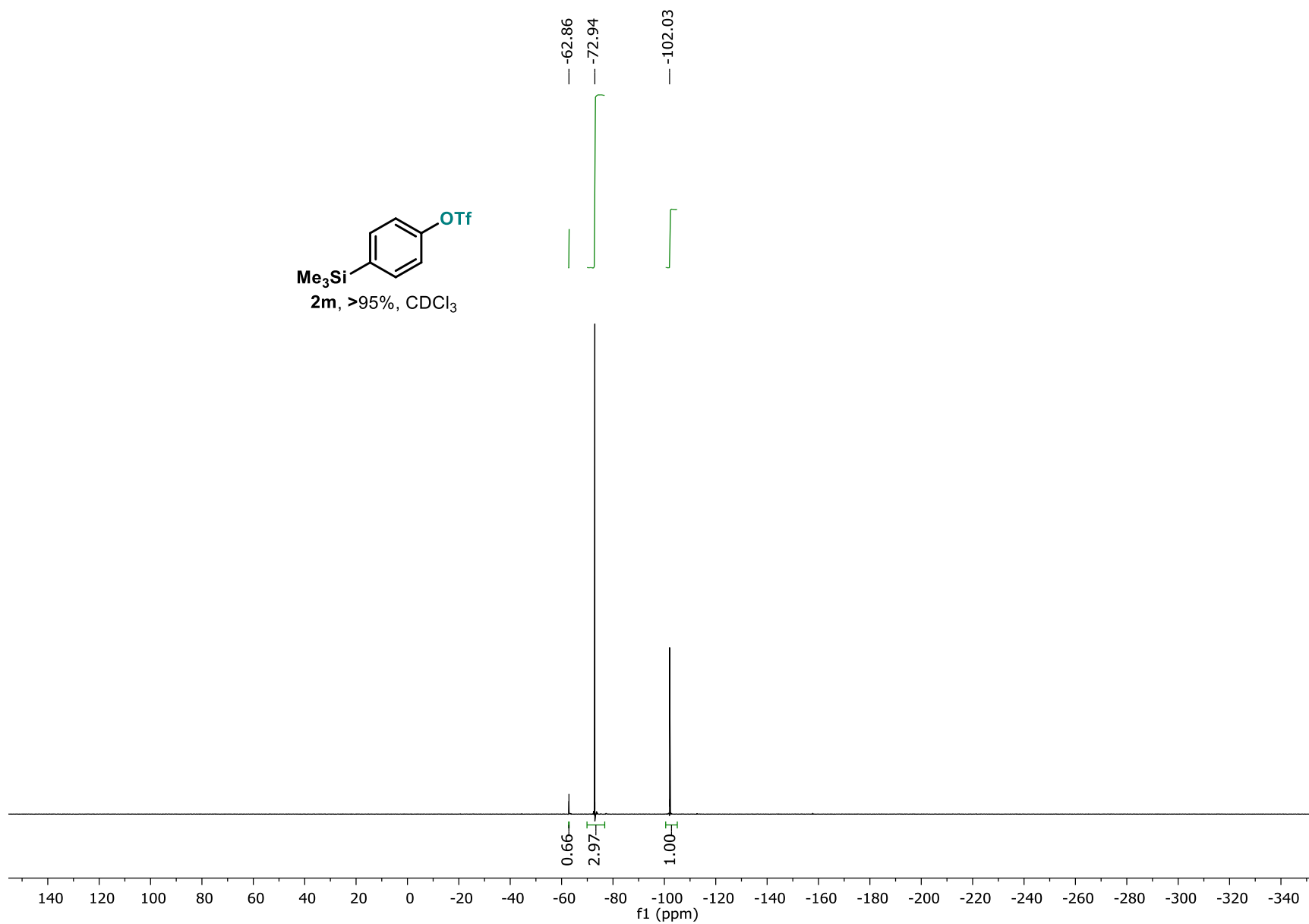
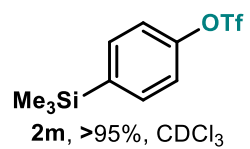


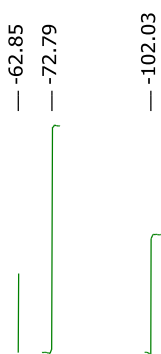
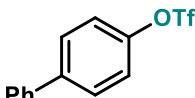


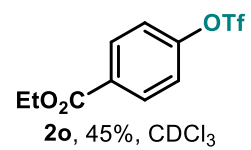


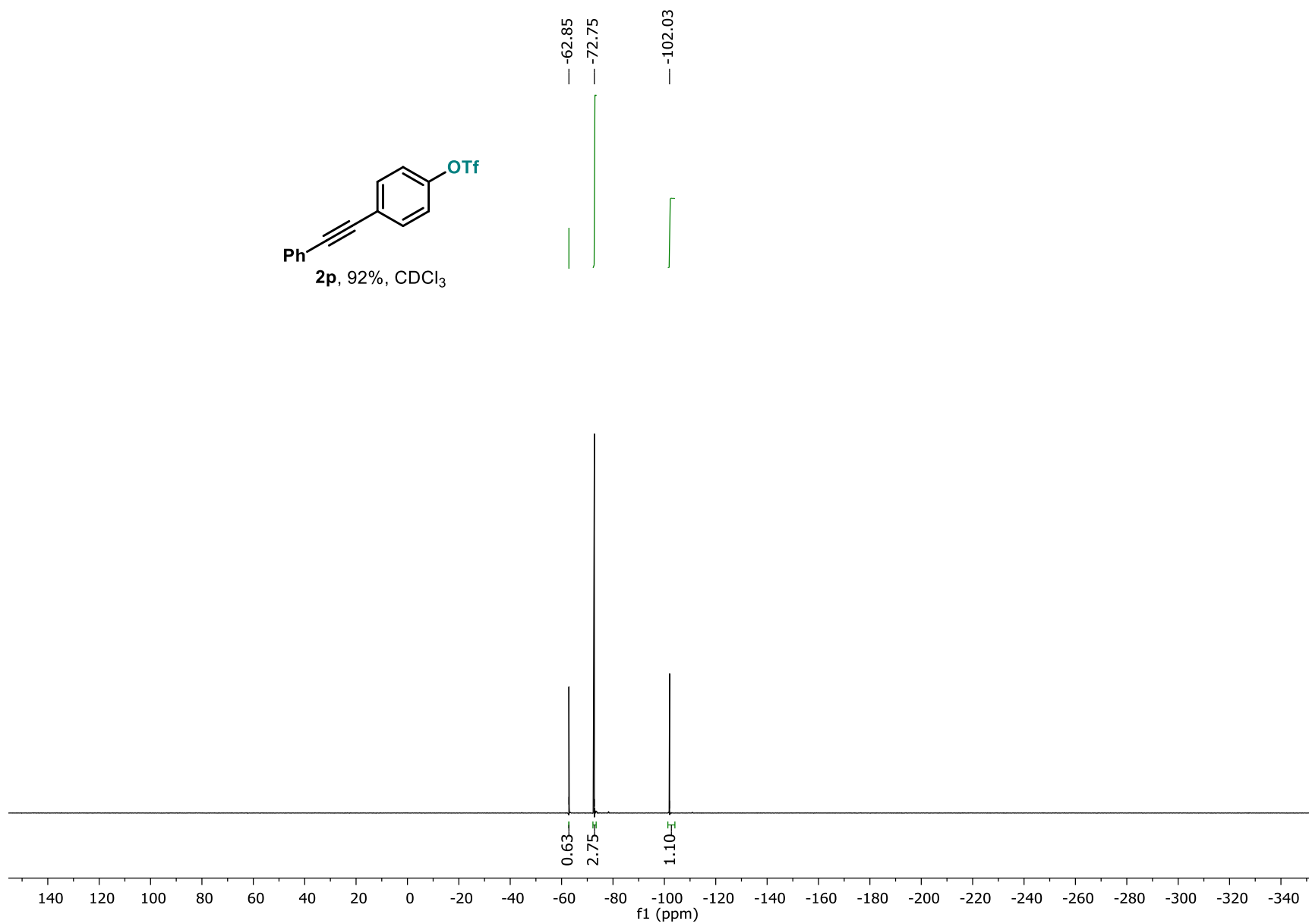
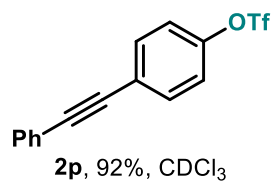


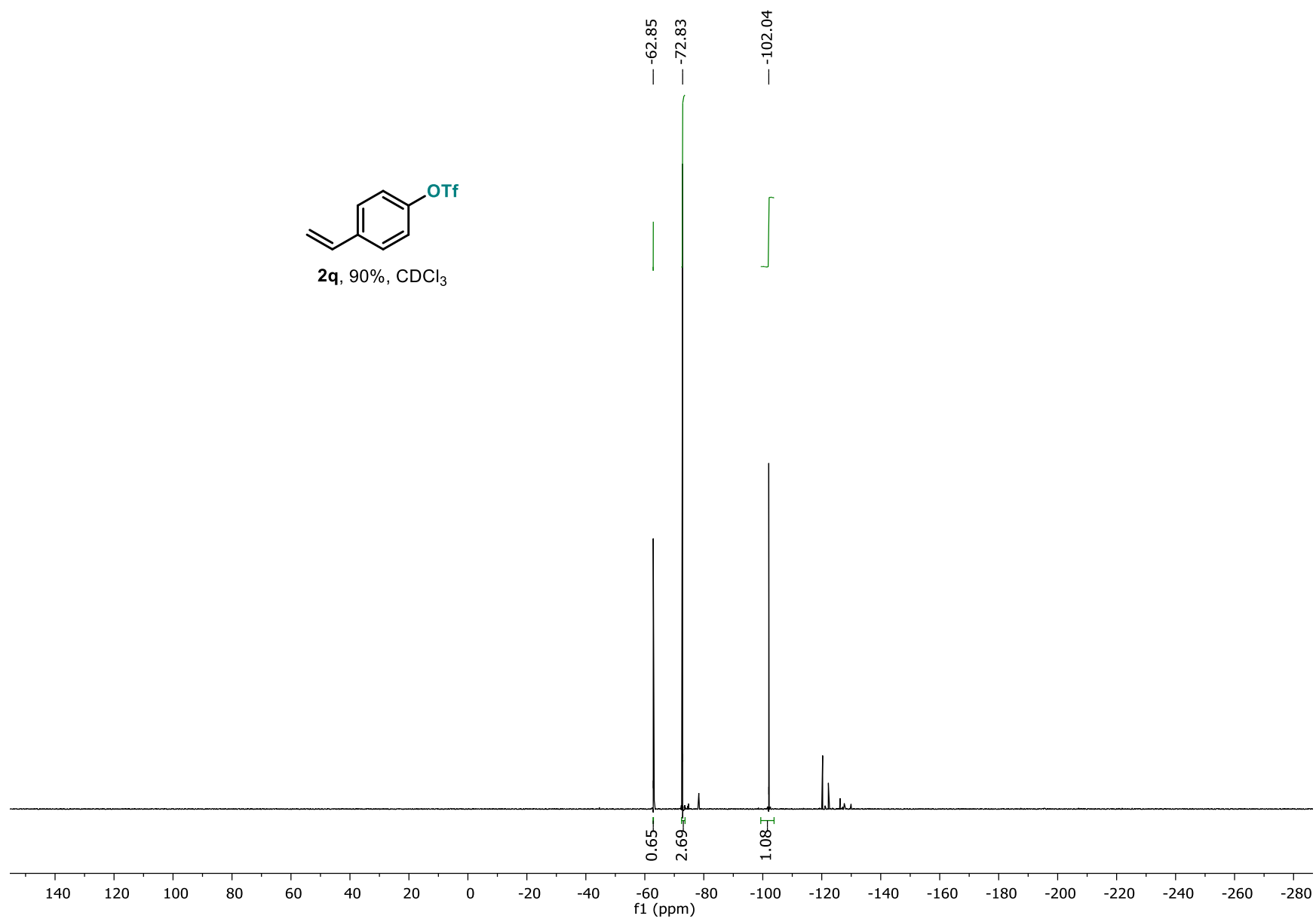
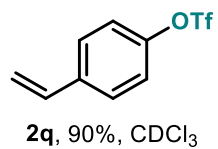


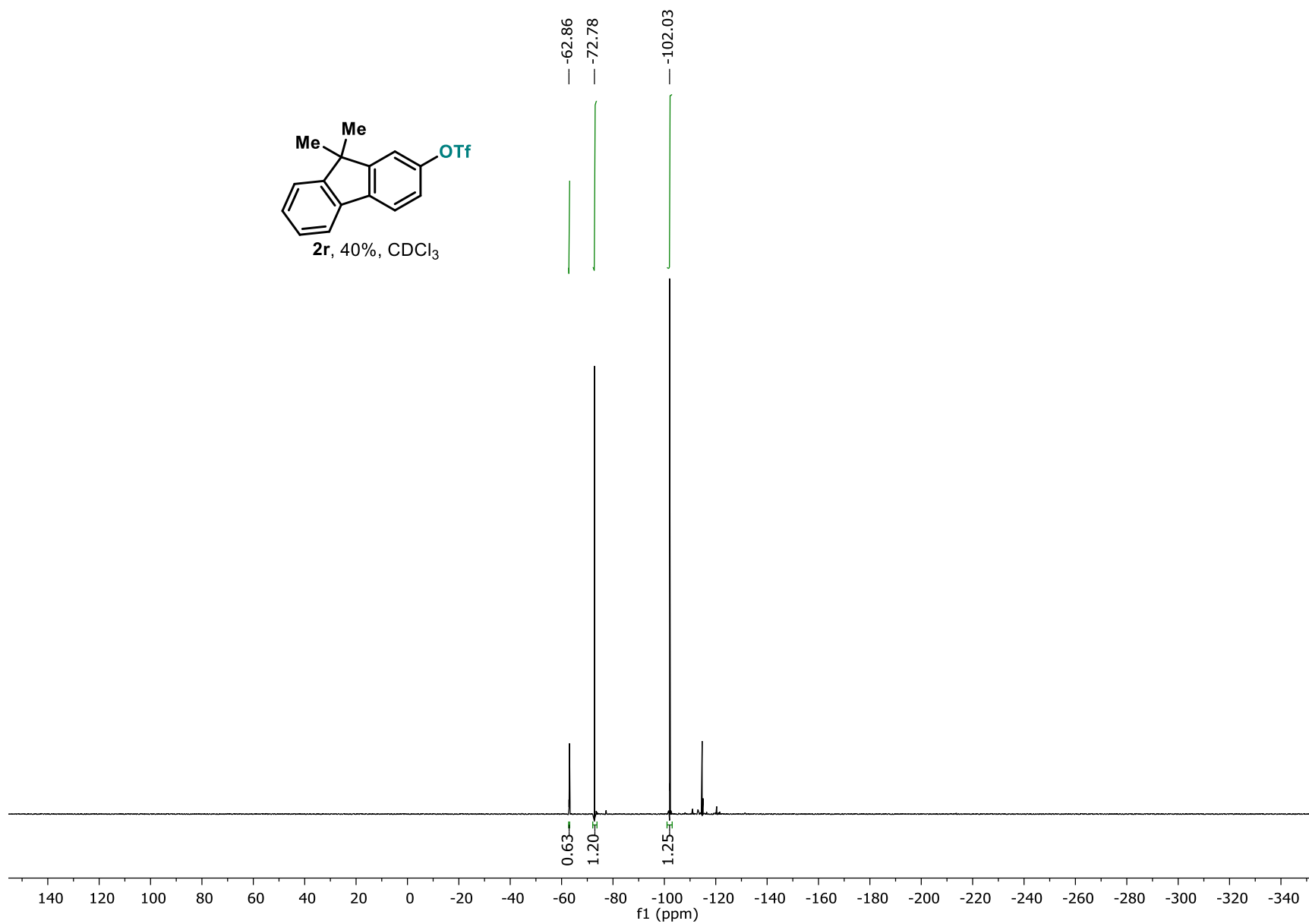
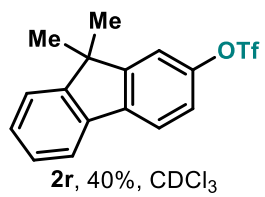


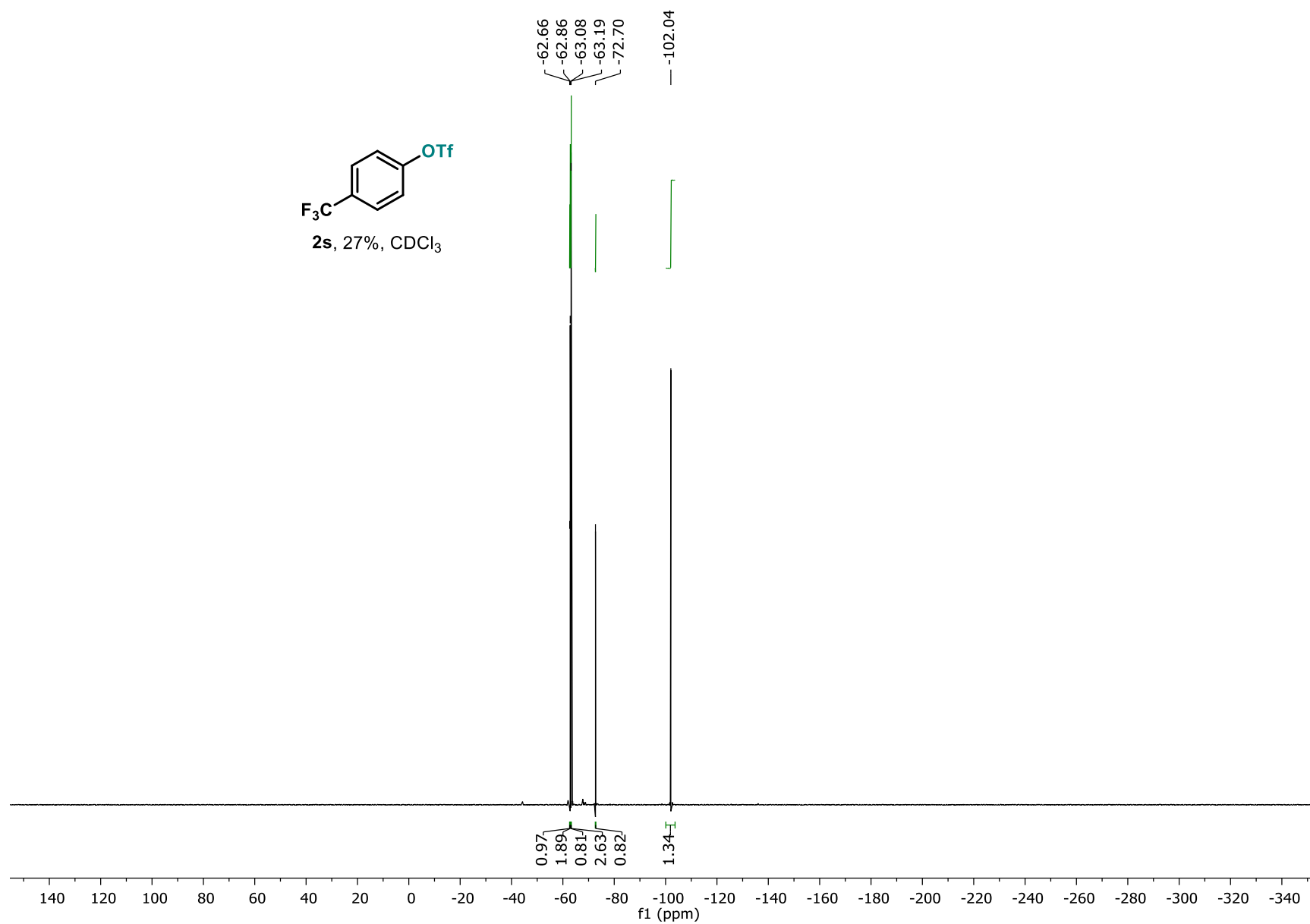
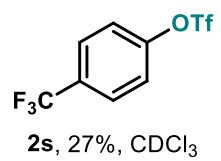






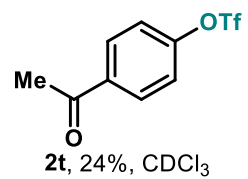




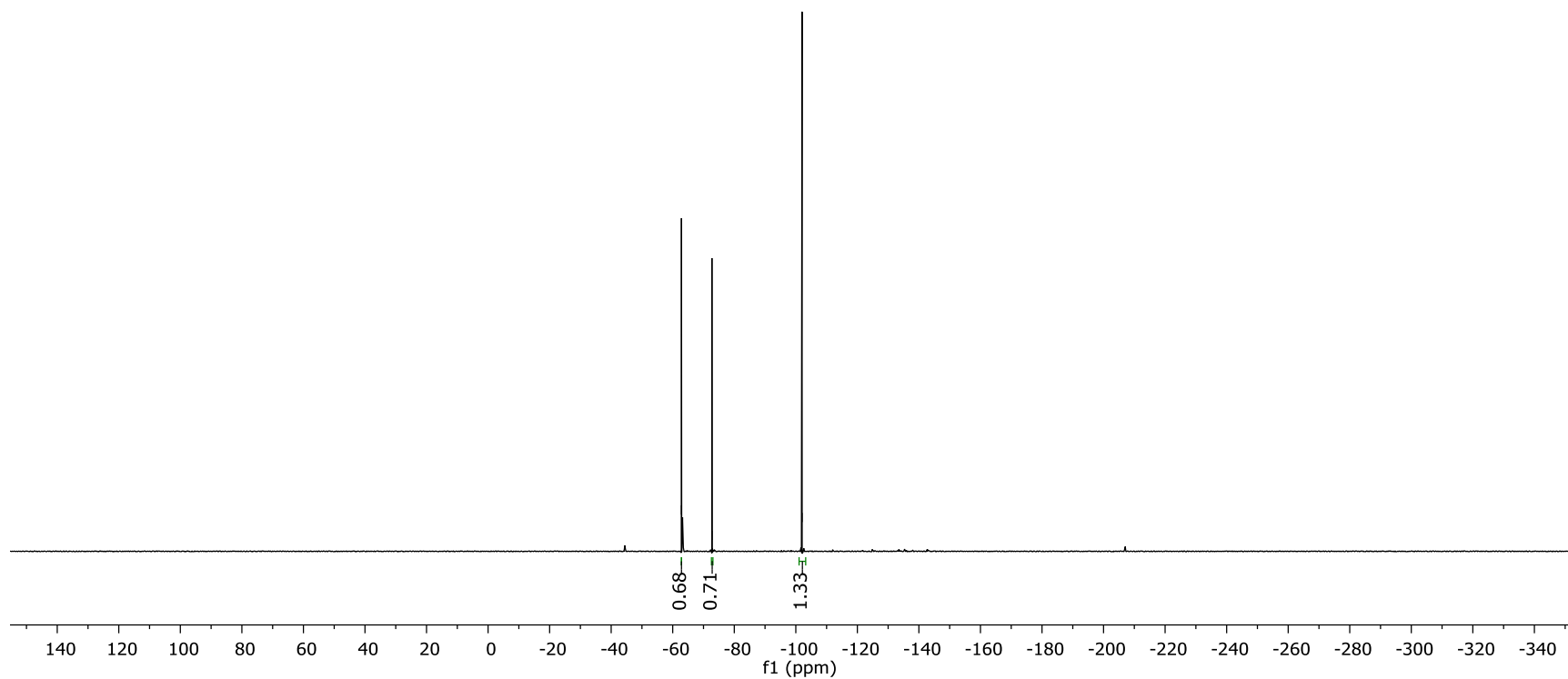


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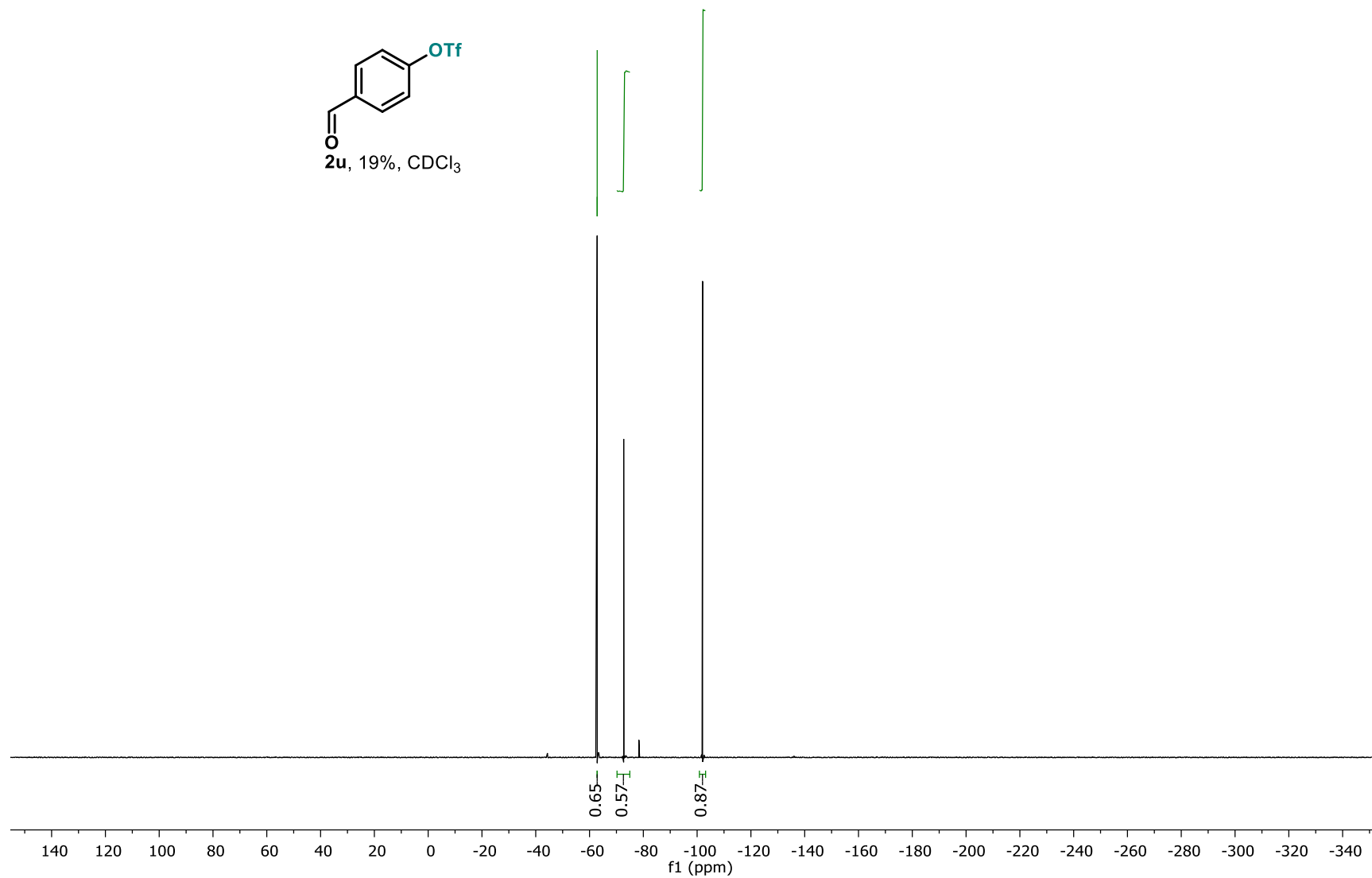
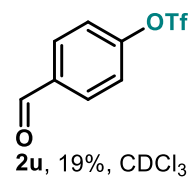




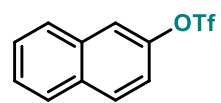
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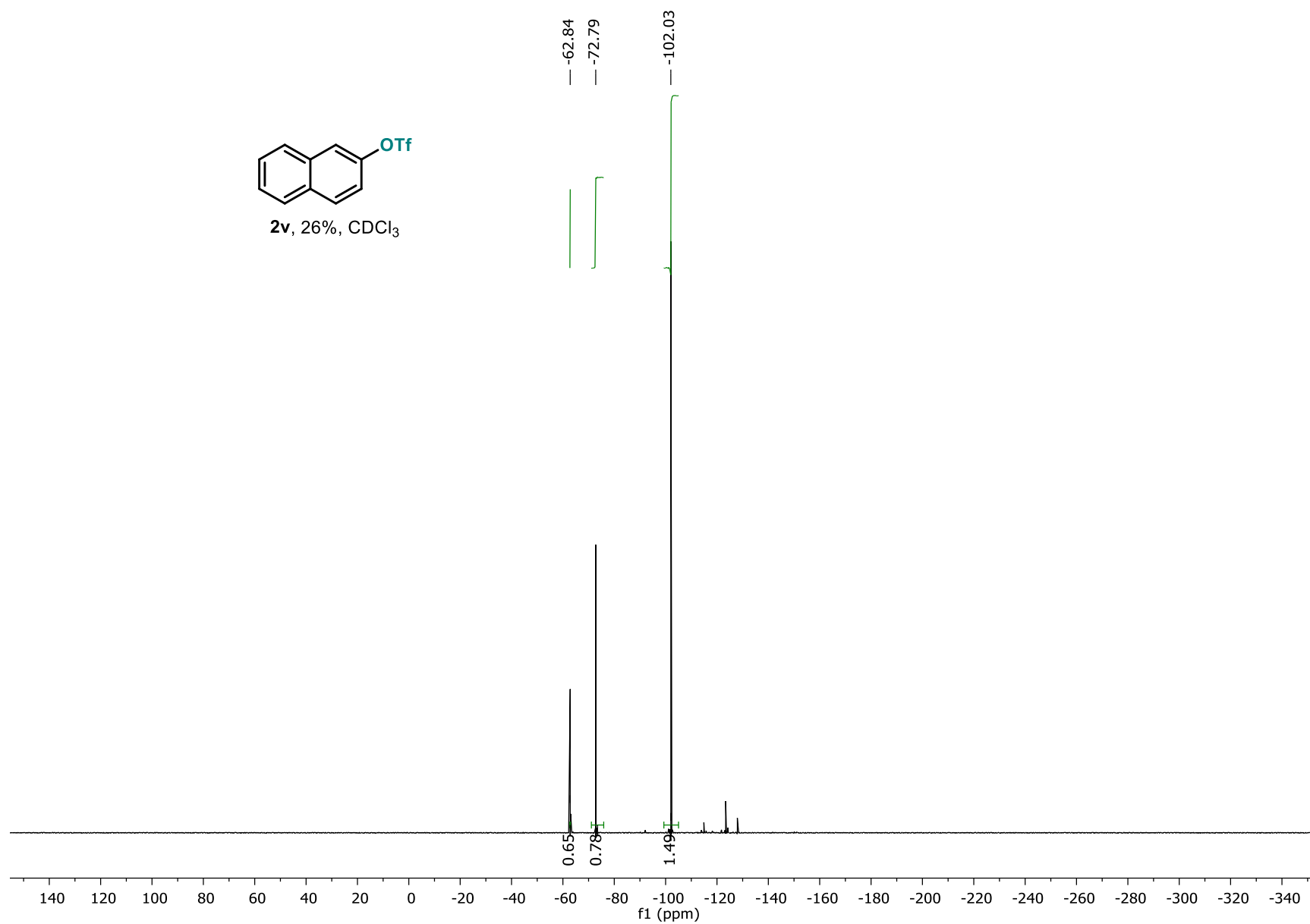
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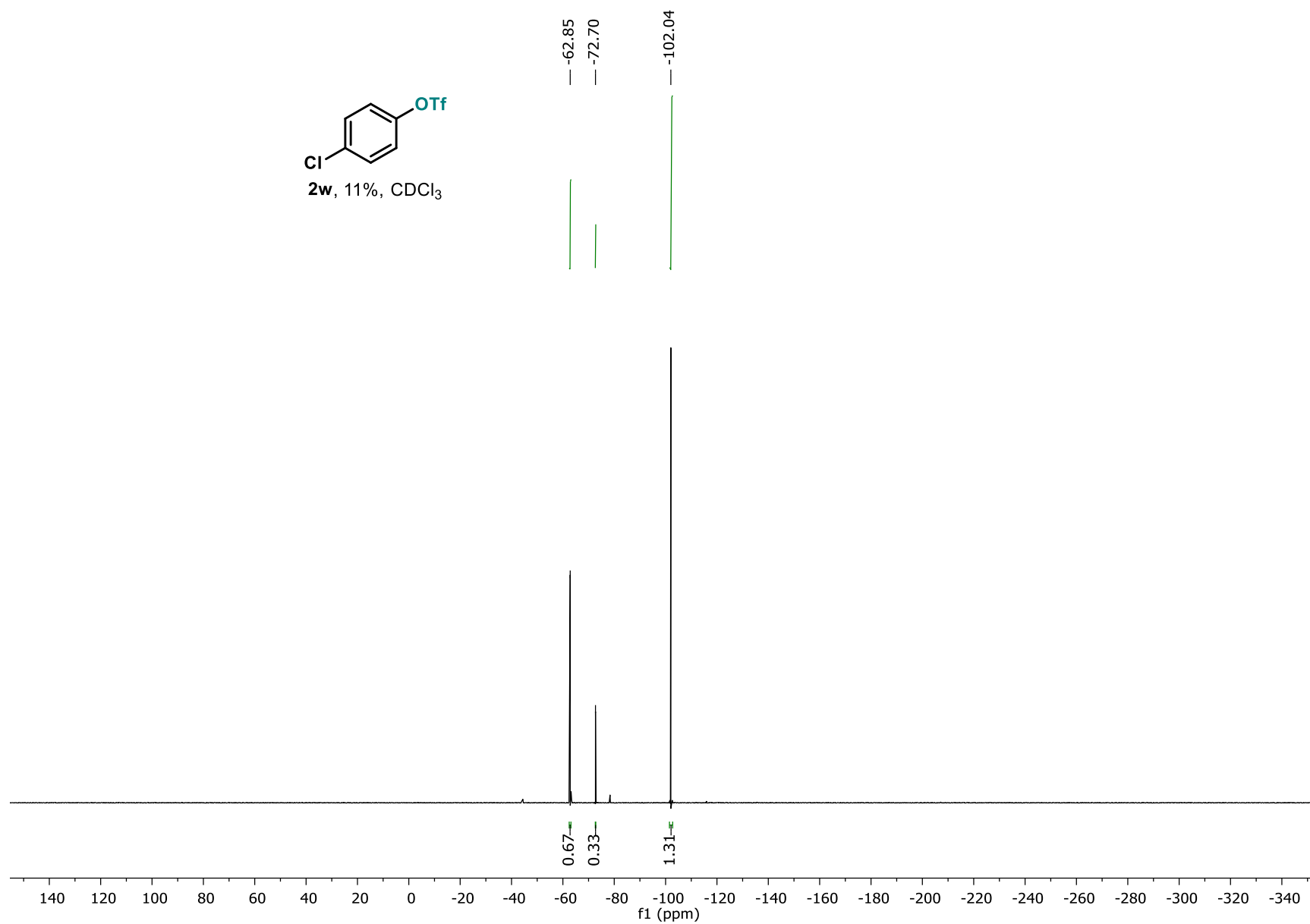
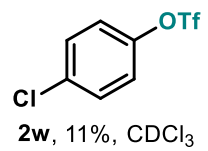


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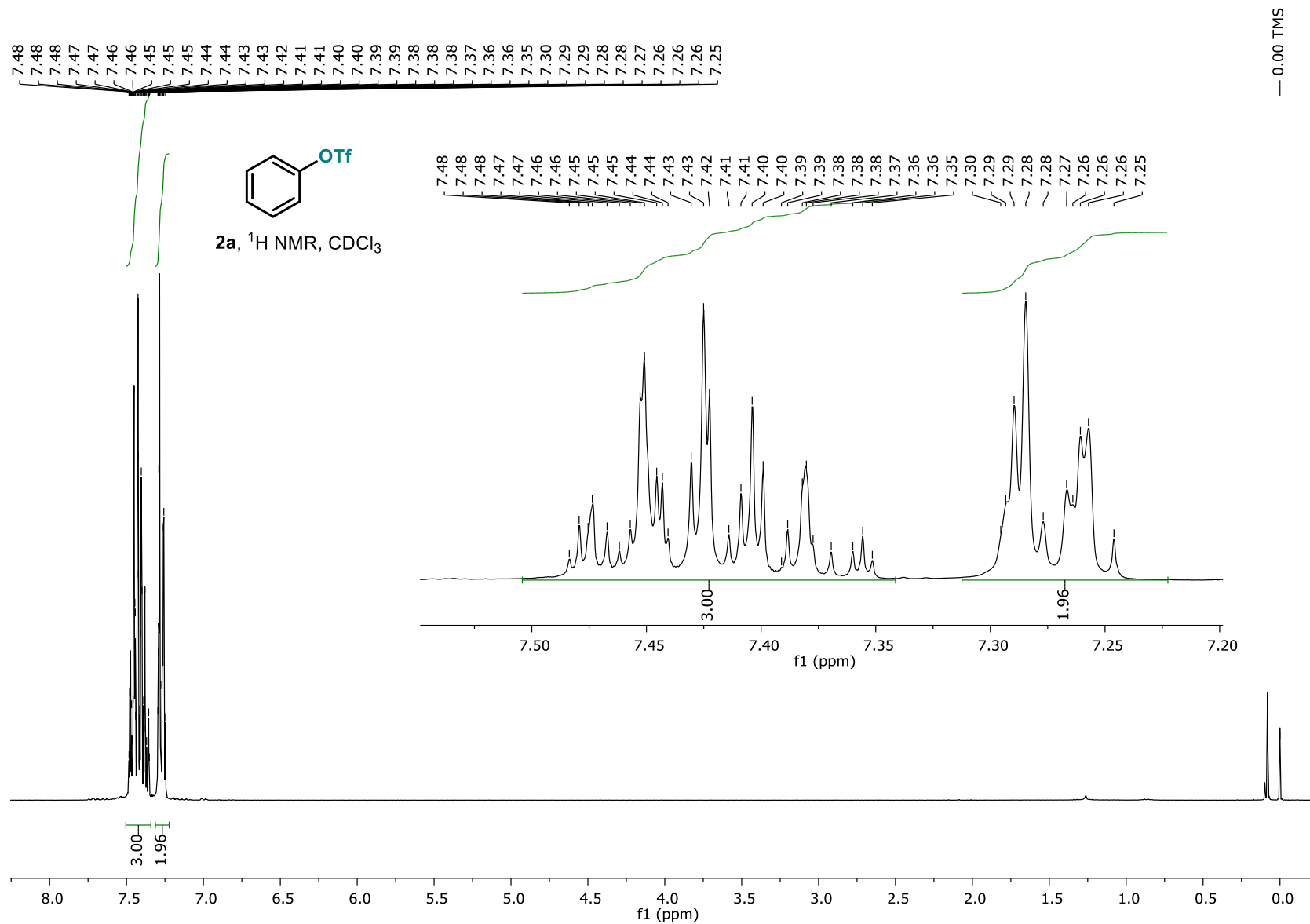
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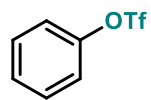




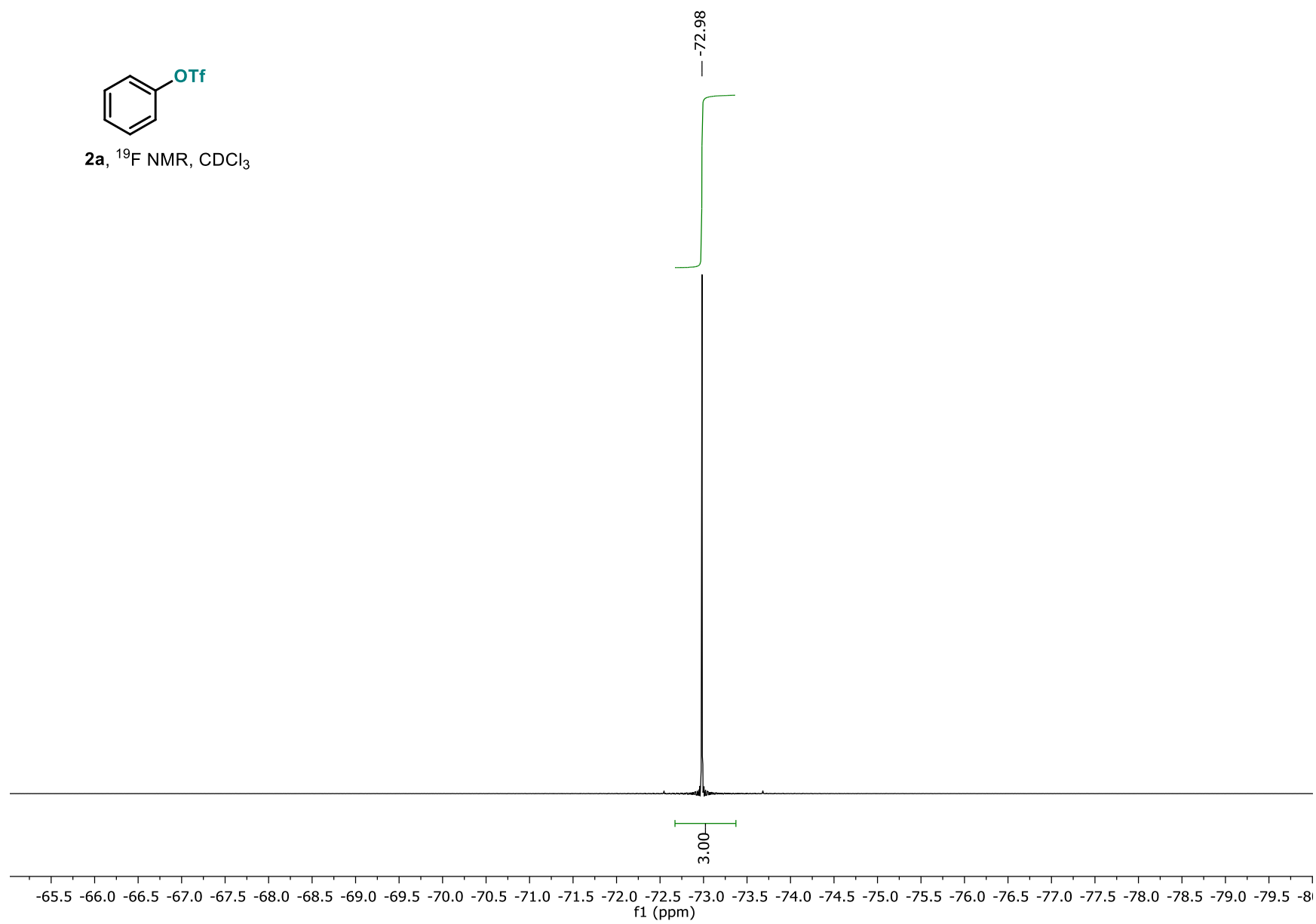
S104

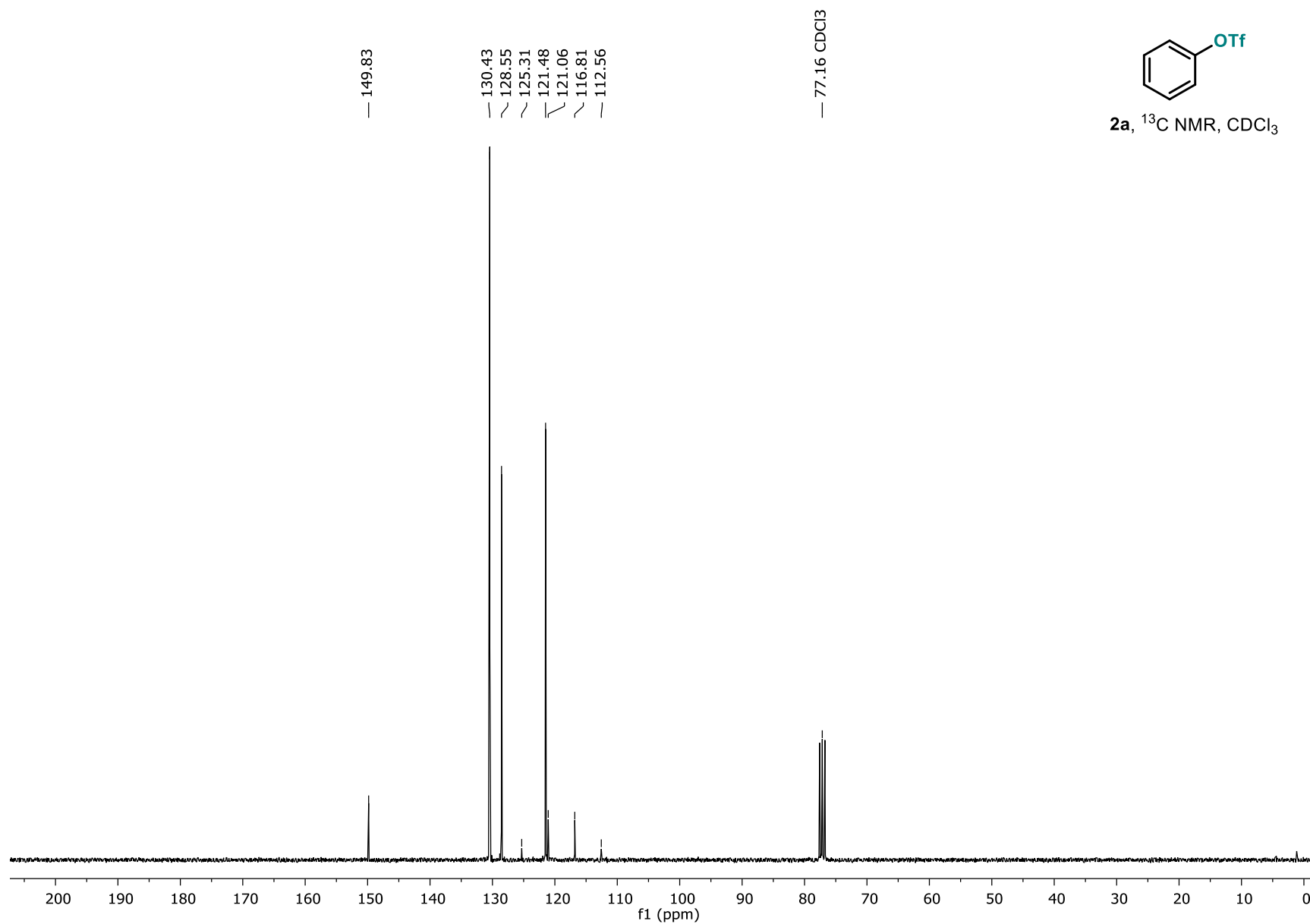
## 11. NMR characterization of isolated aryl triflates 2

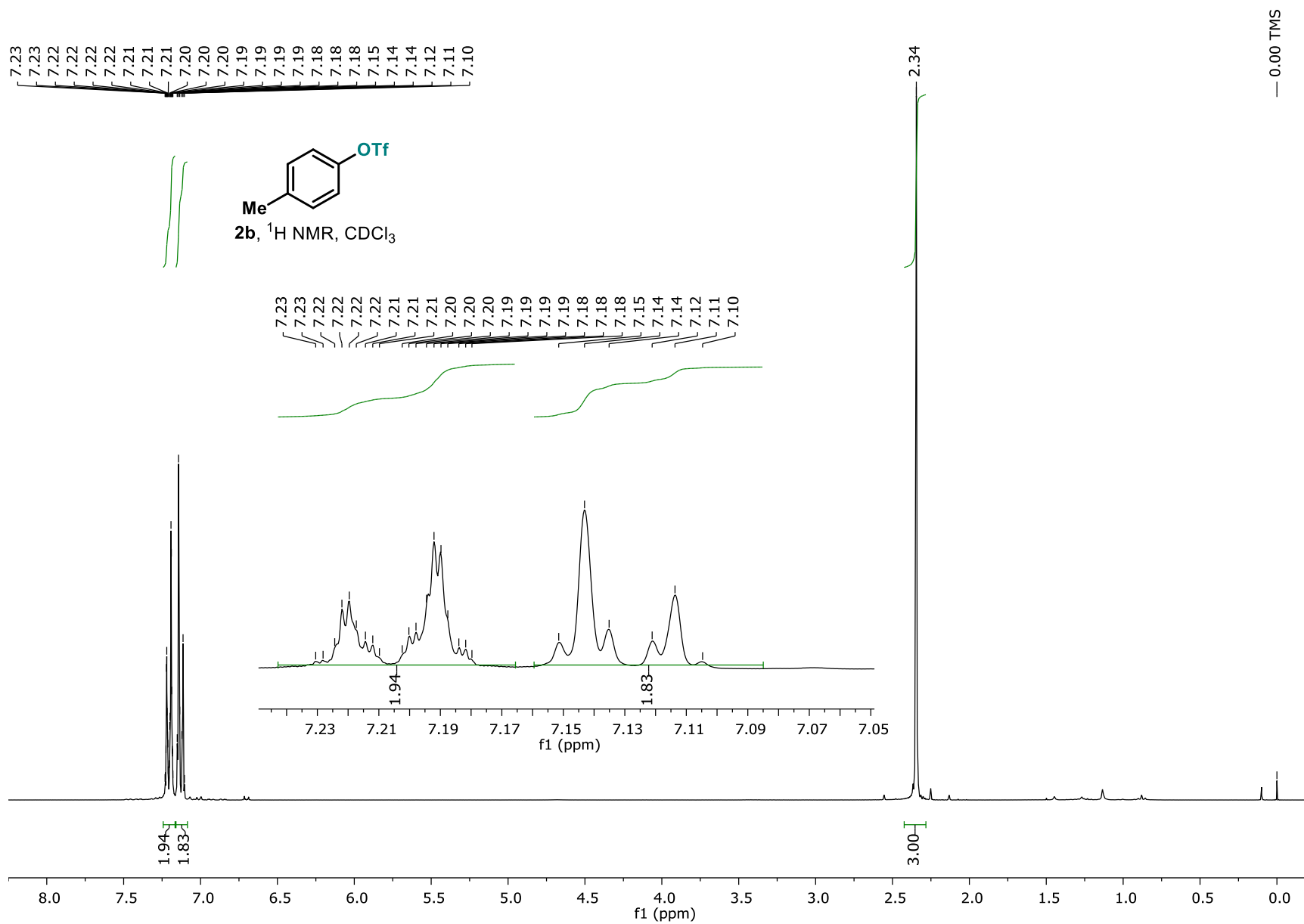




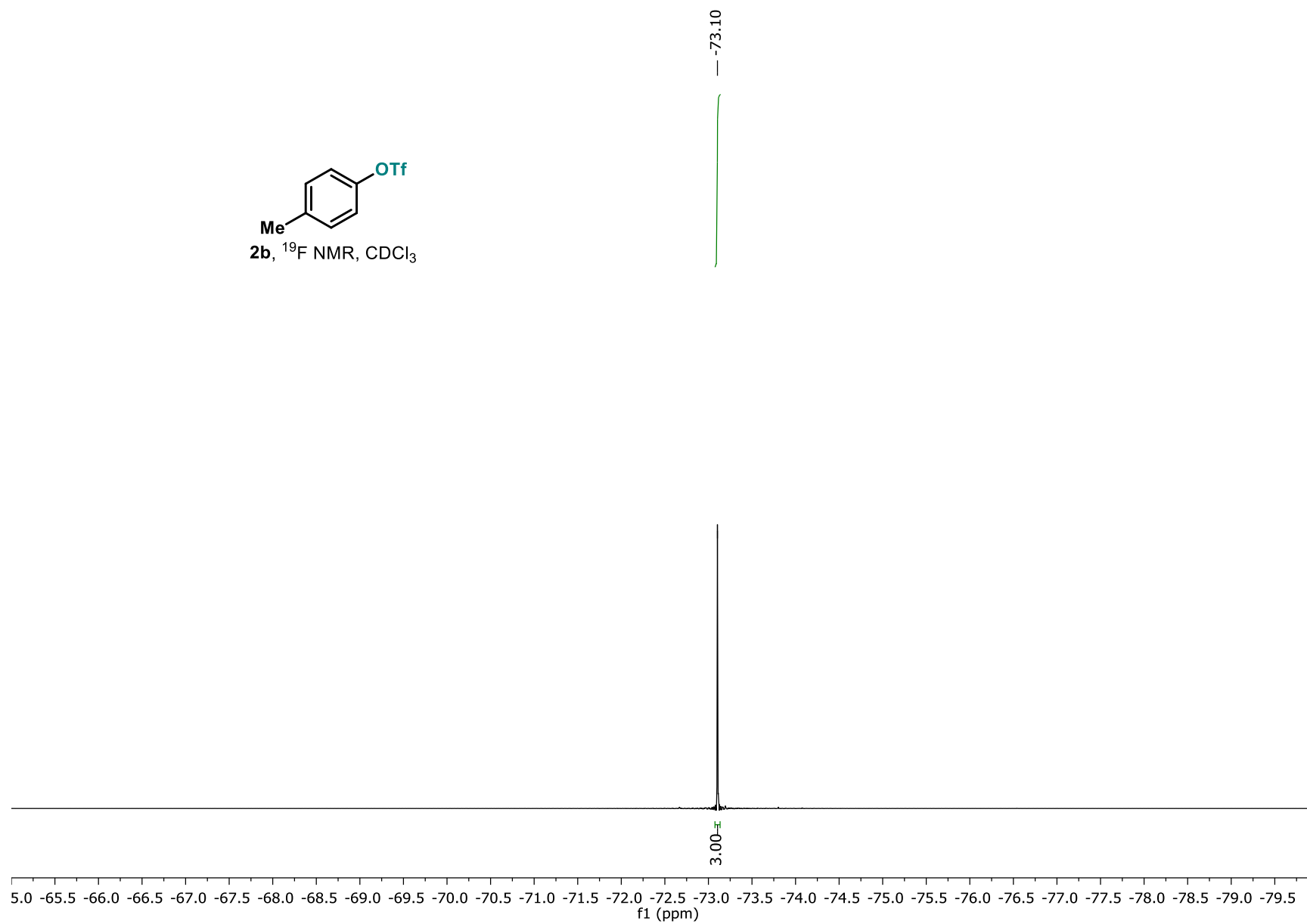
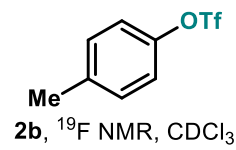
**2a**,  $^{19}\text{F}$  NMR,  $\text{CDCl}_3$

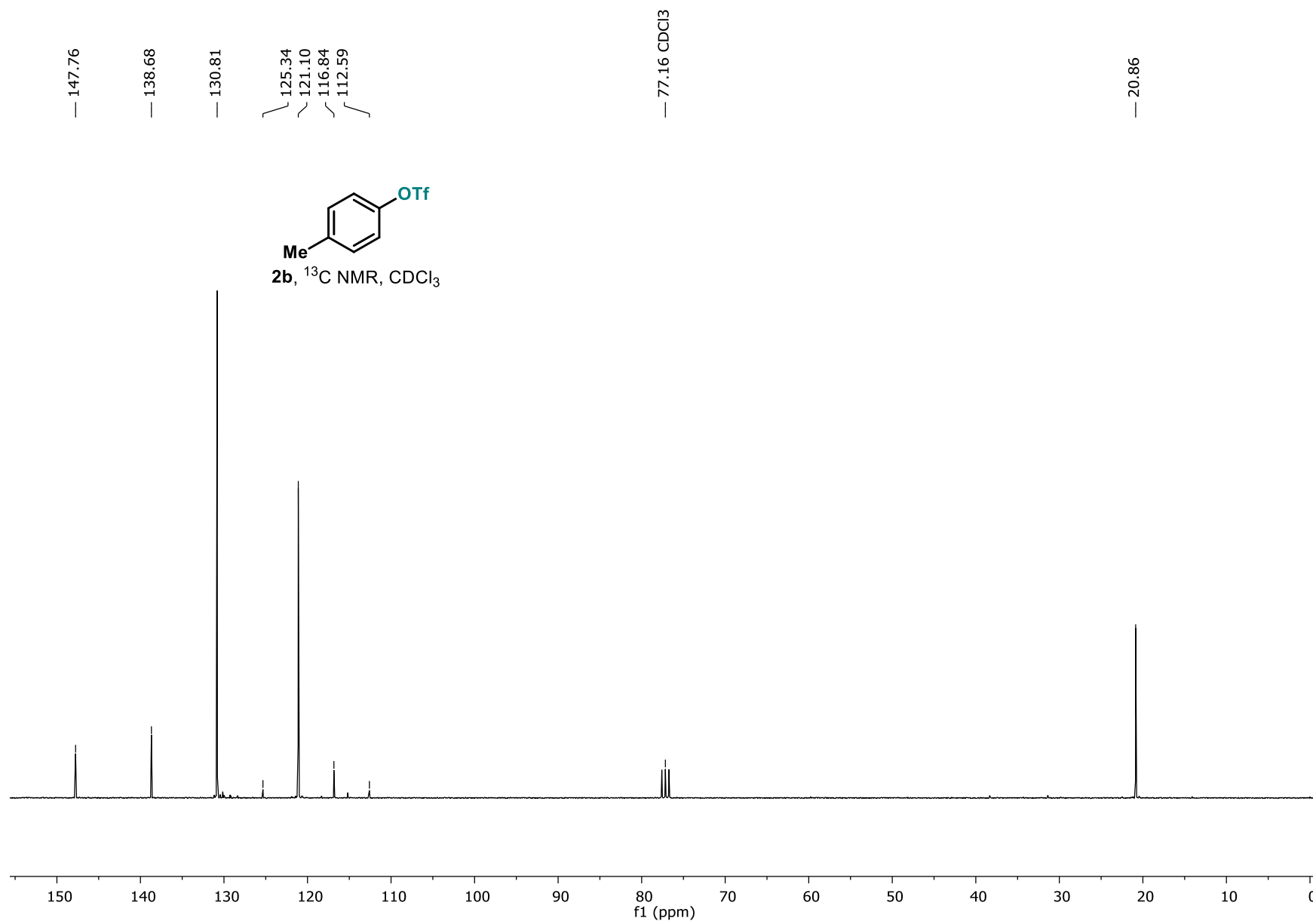


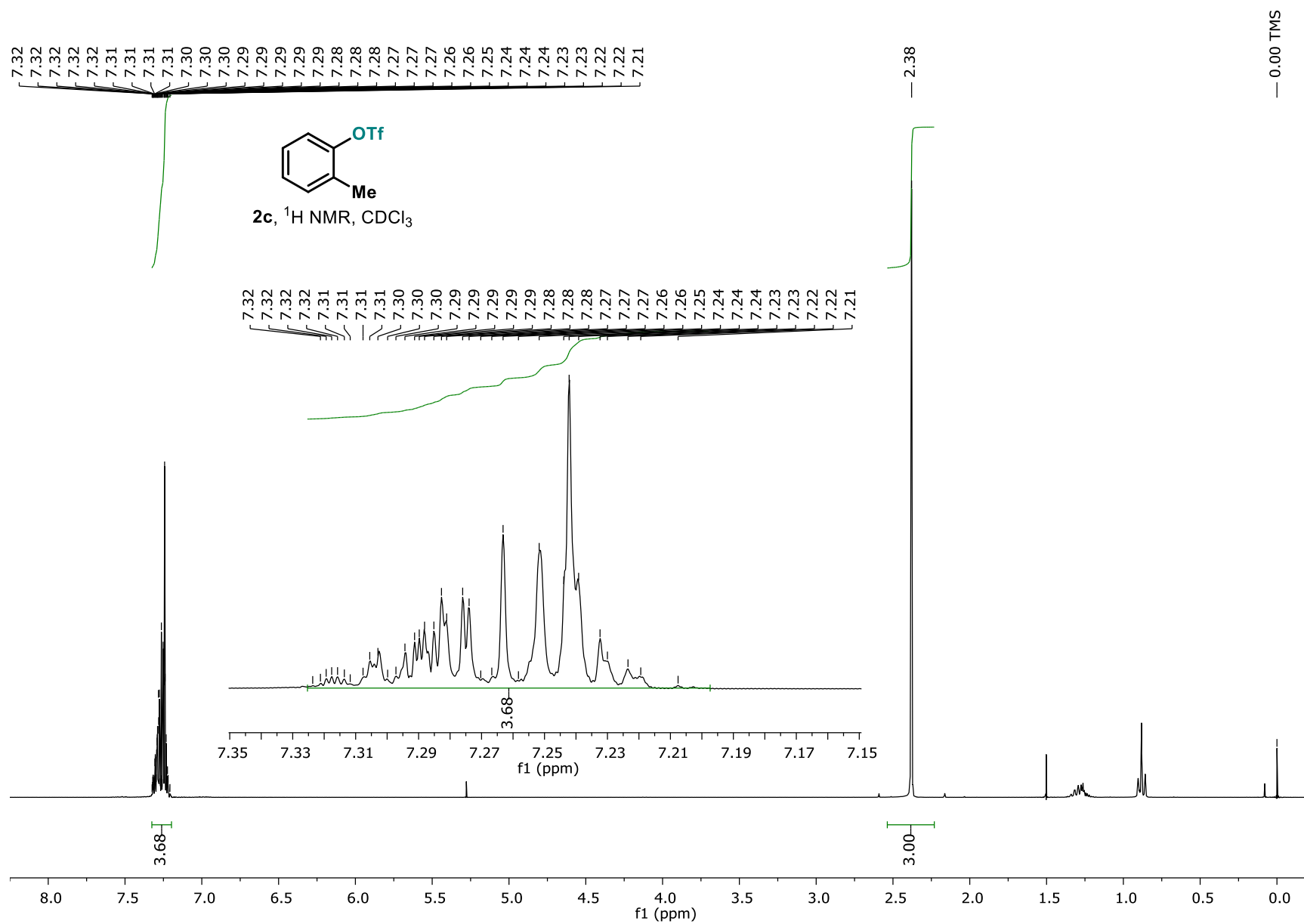


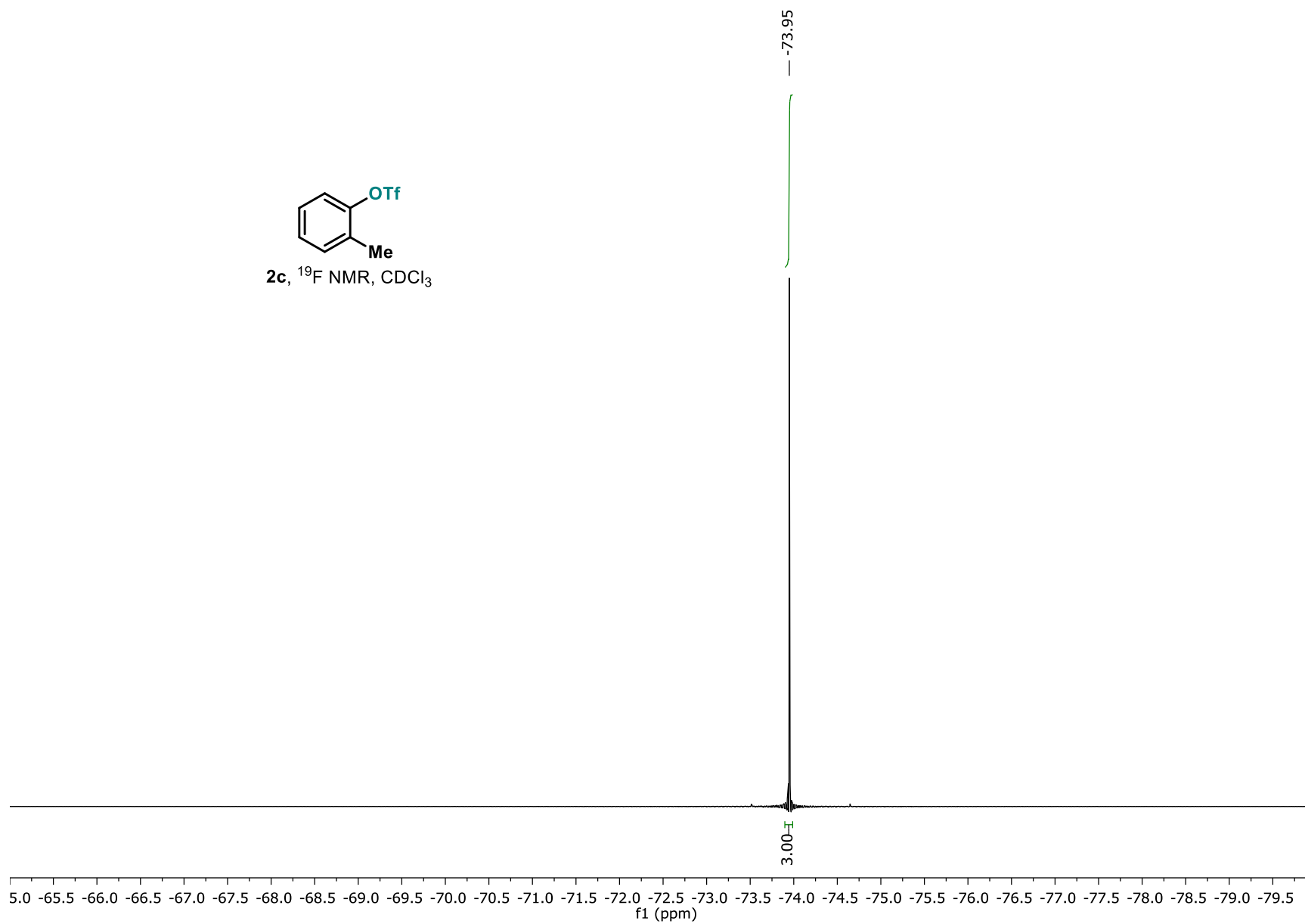
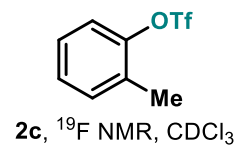


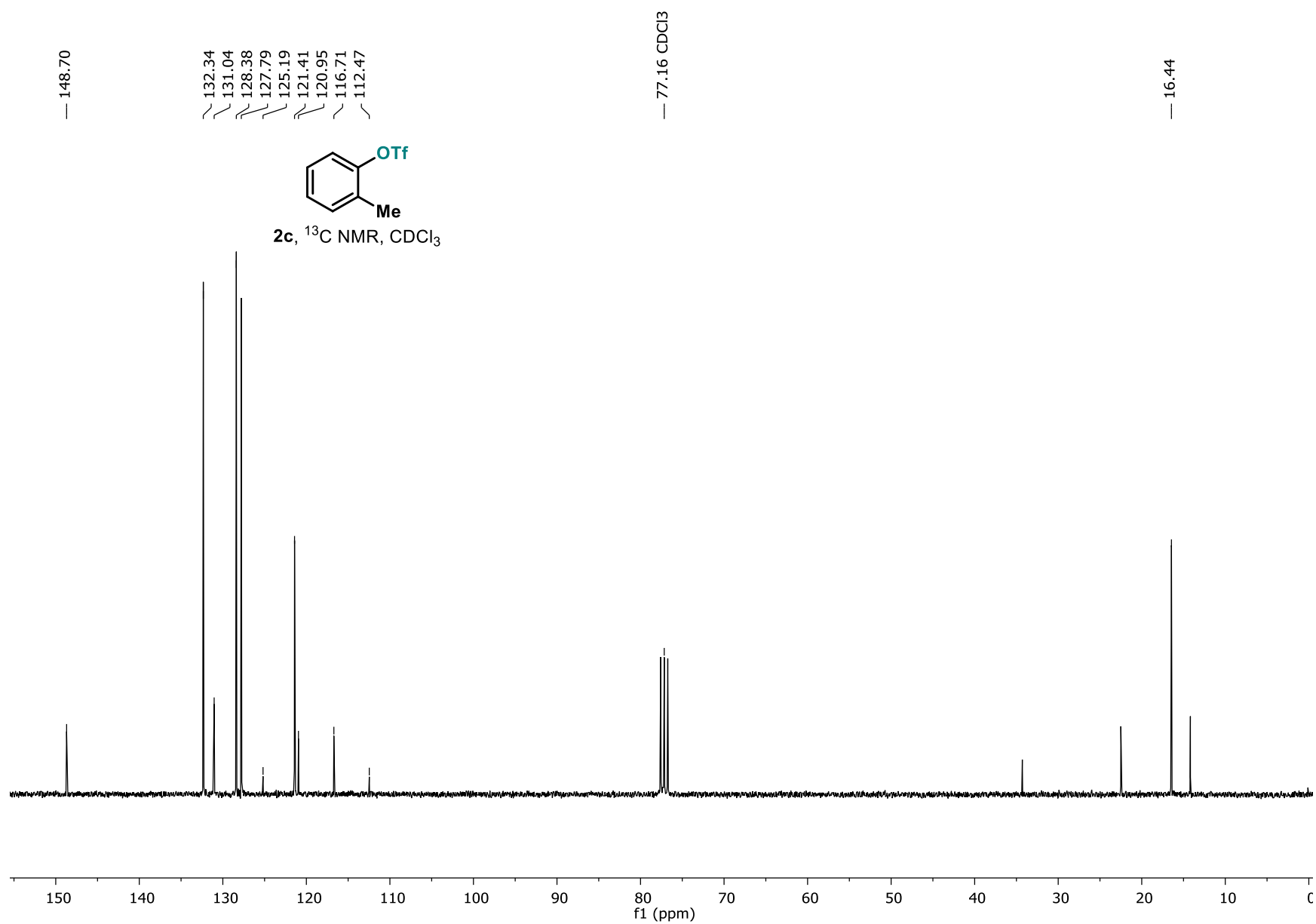


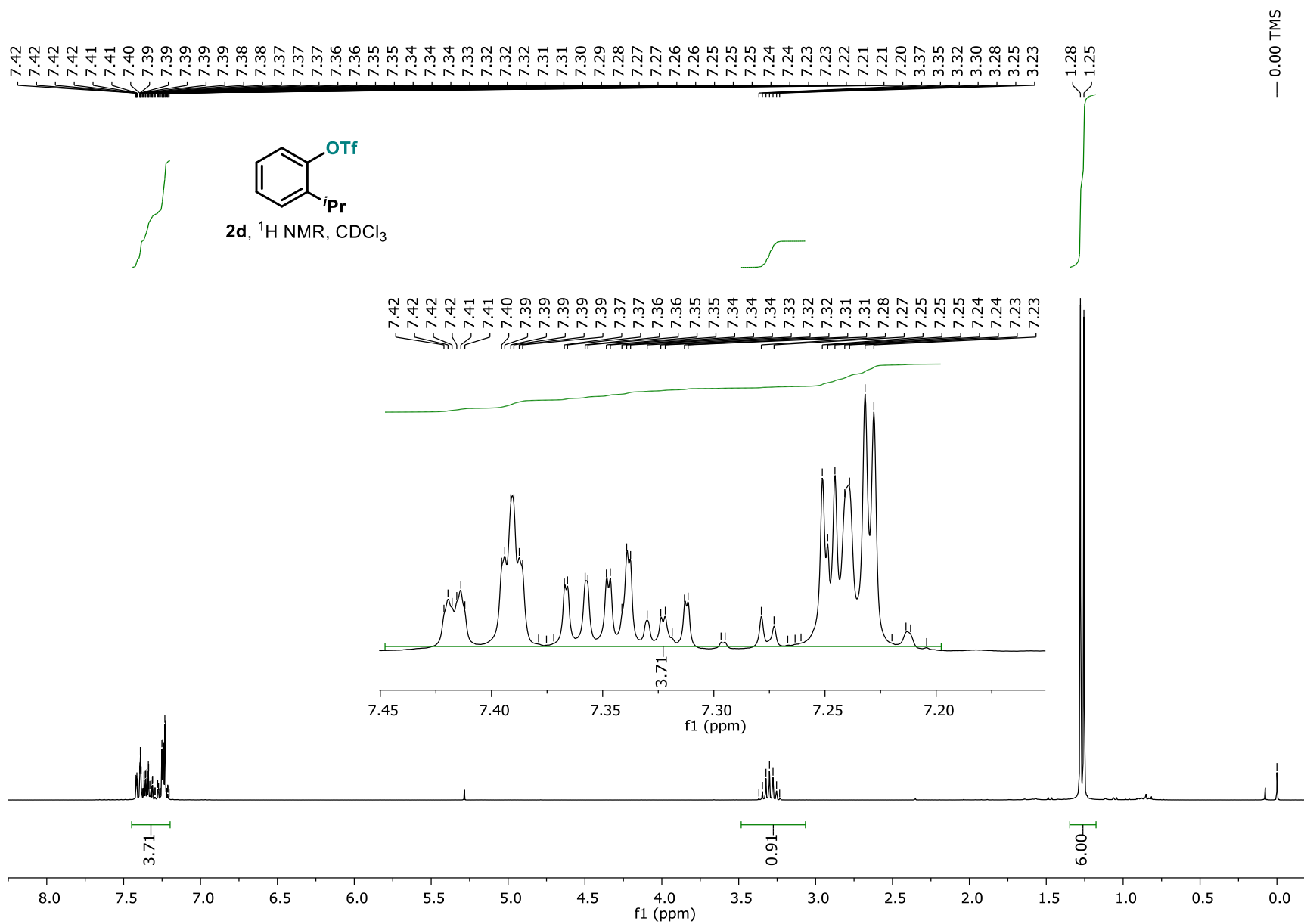


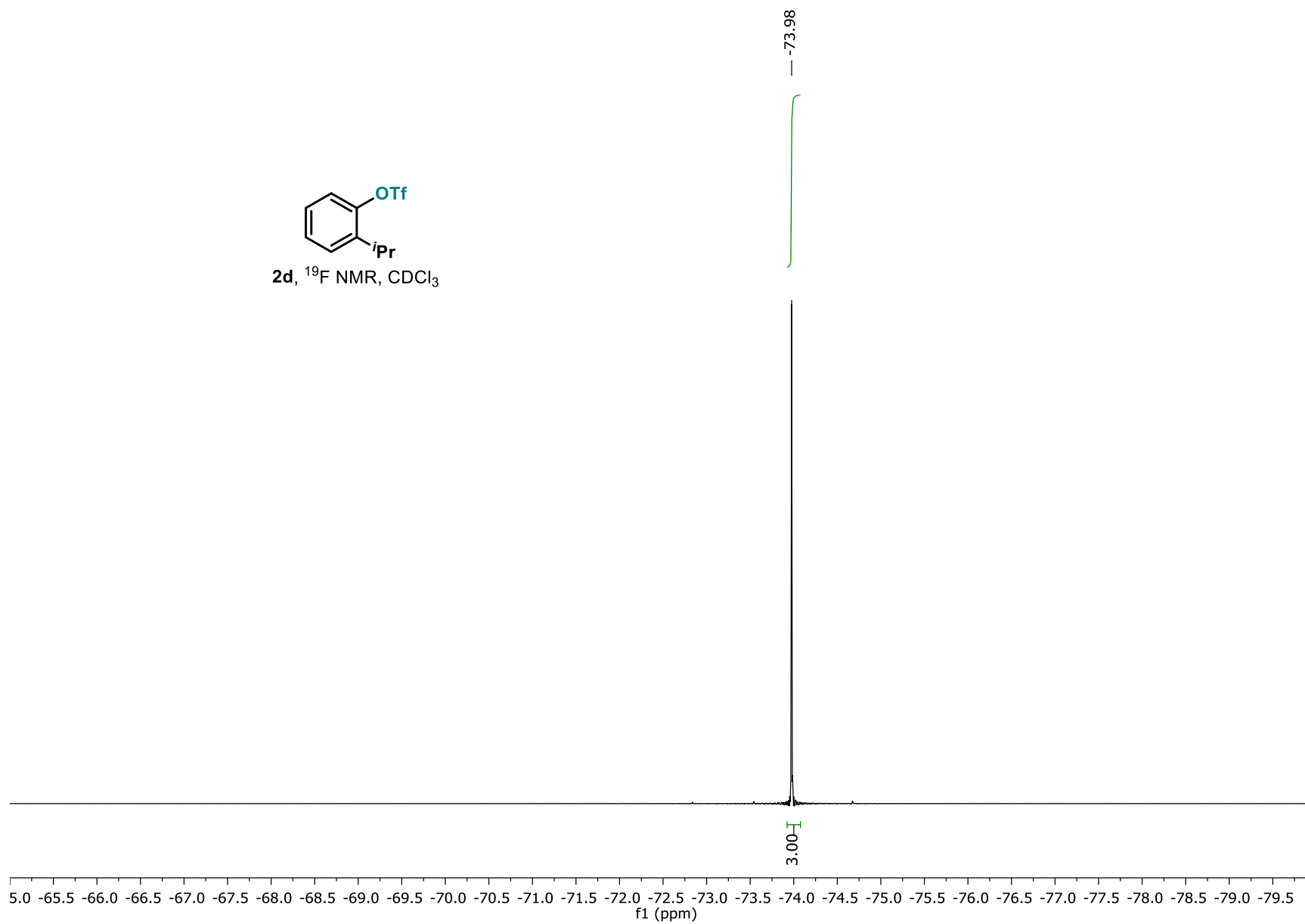
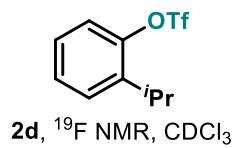


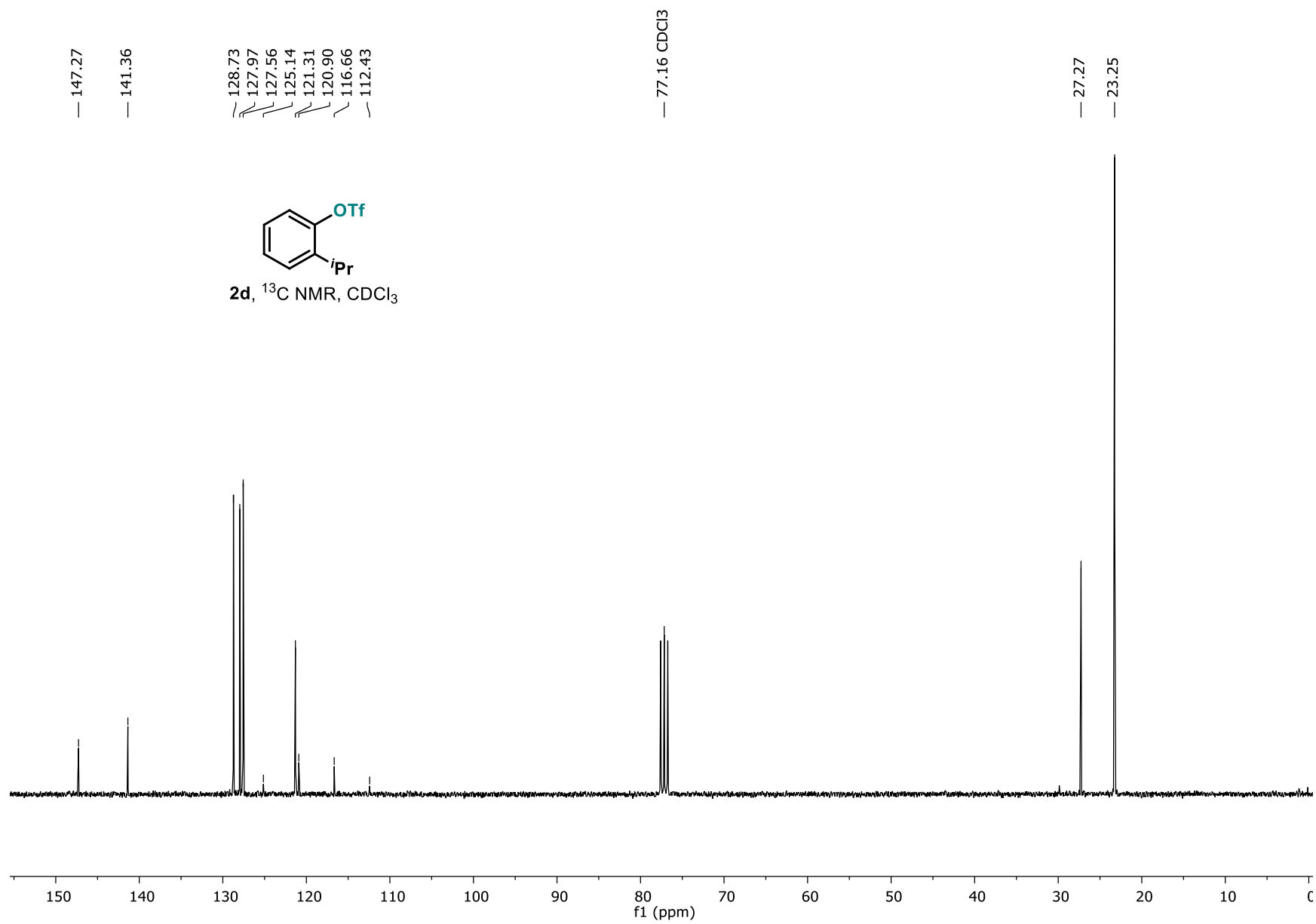




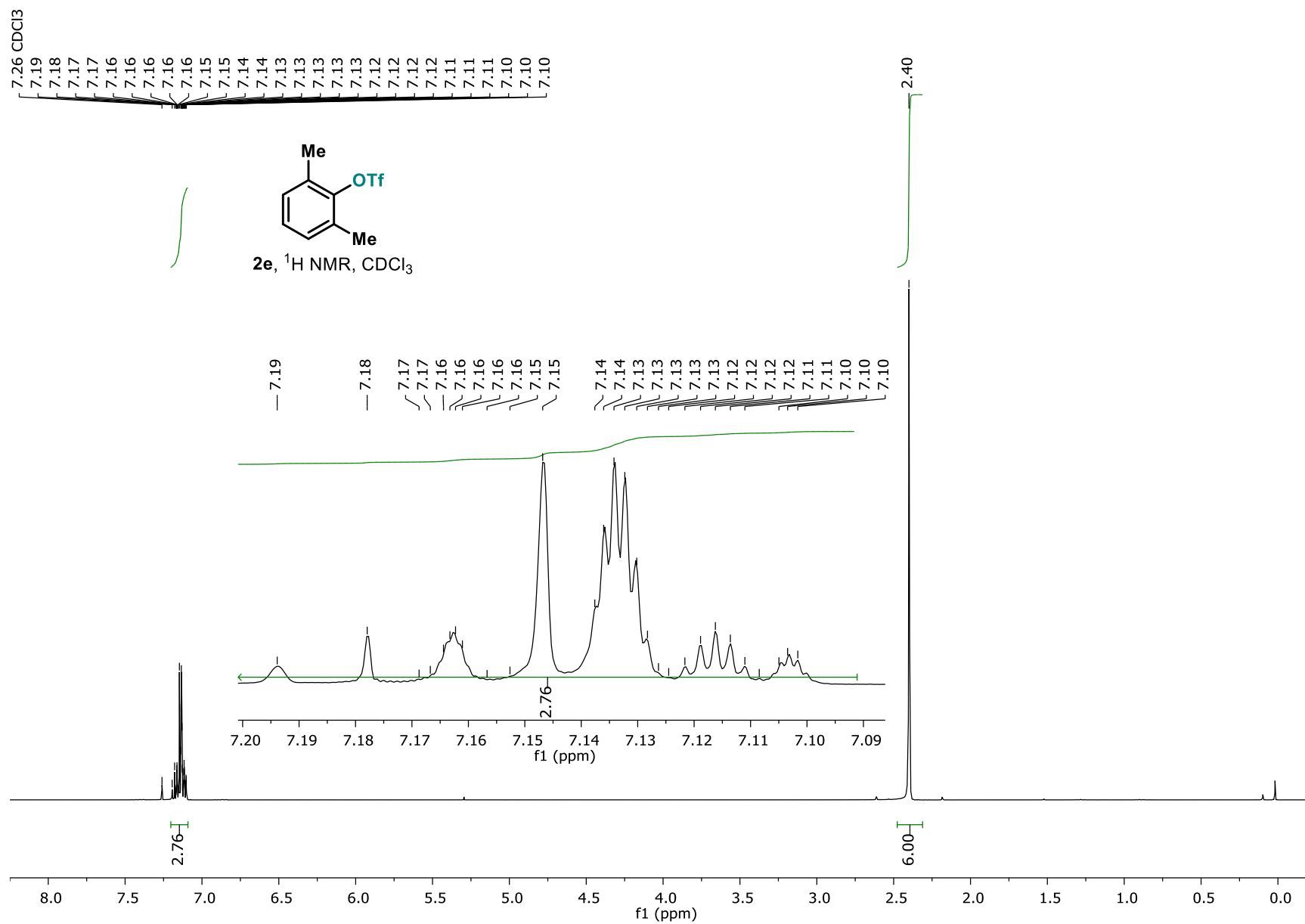


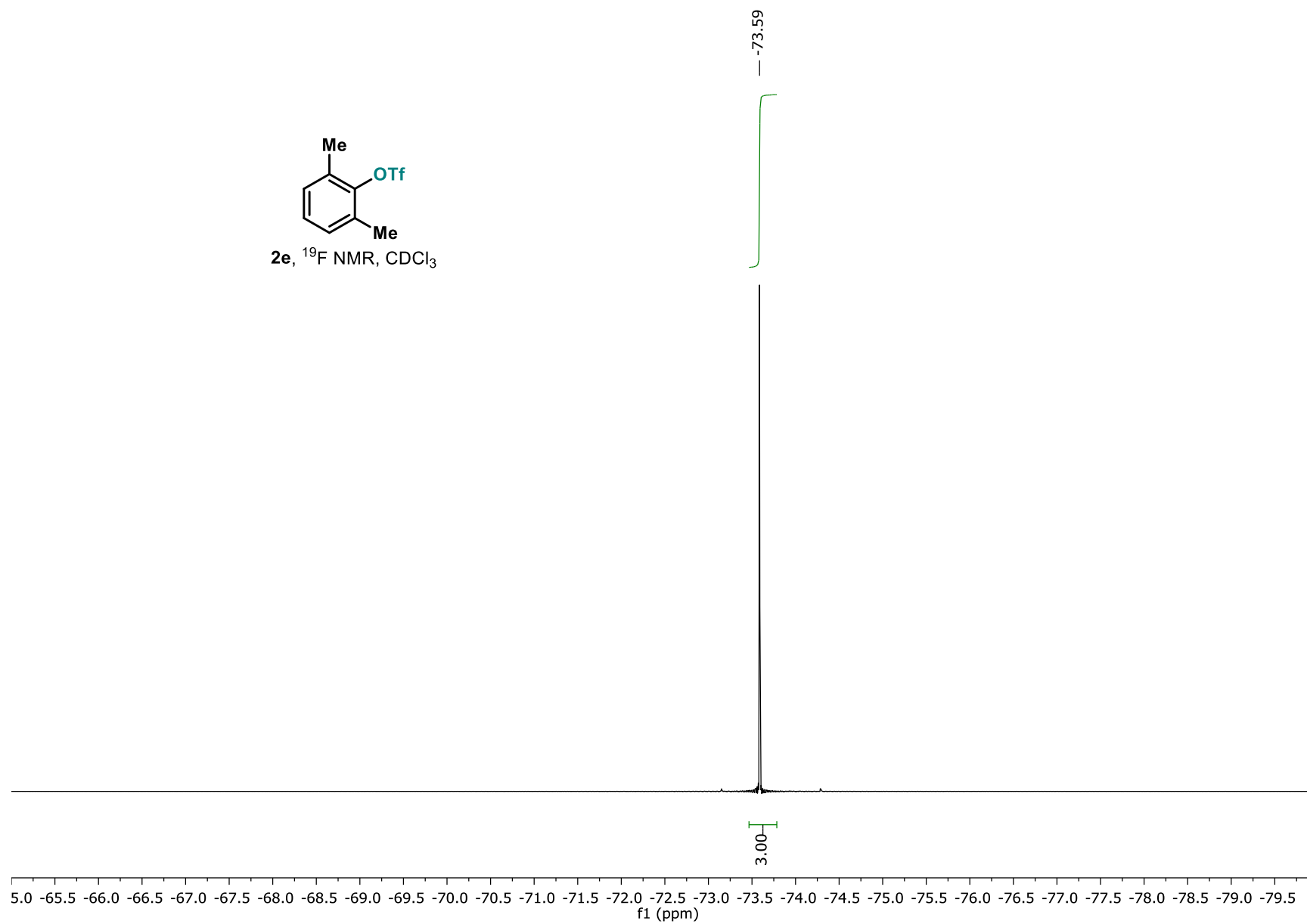
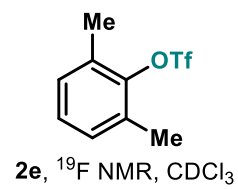




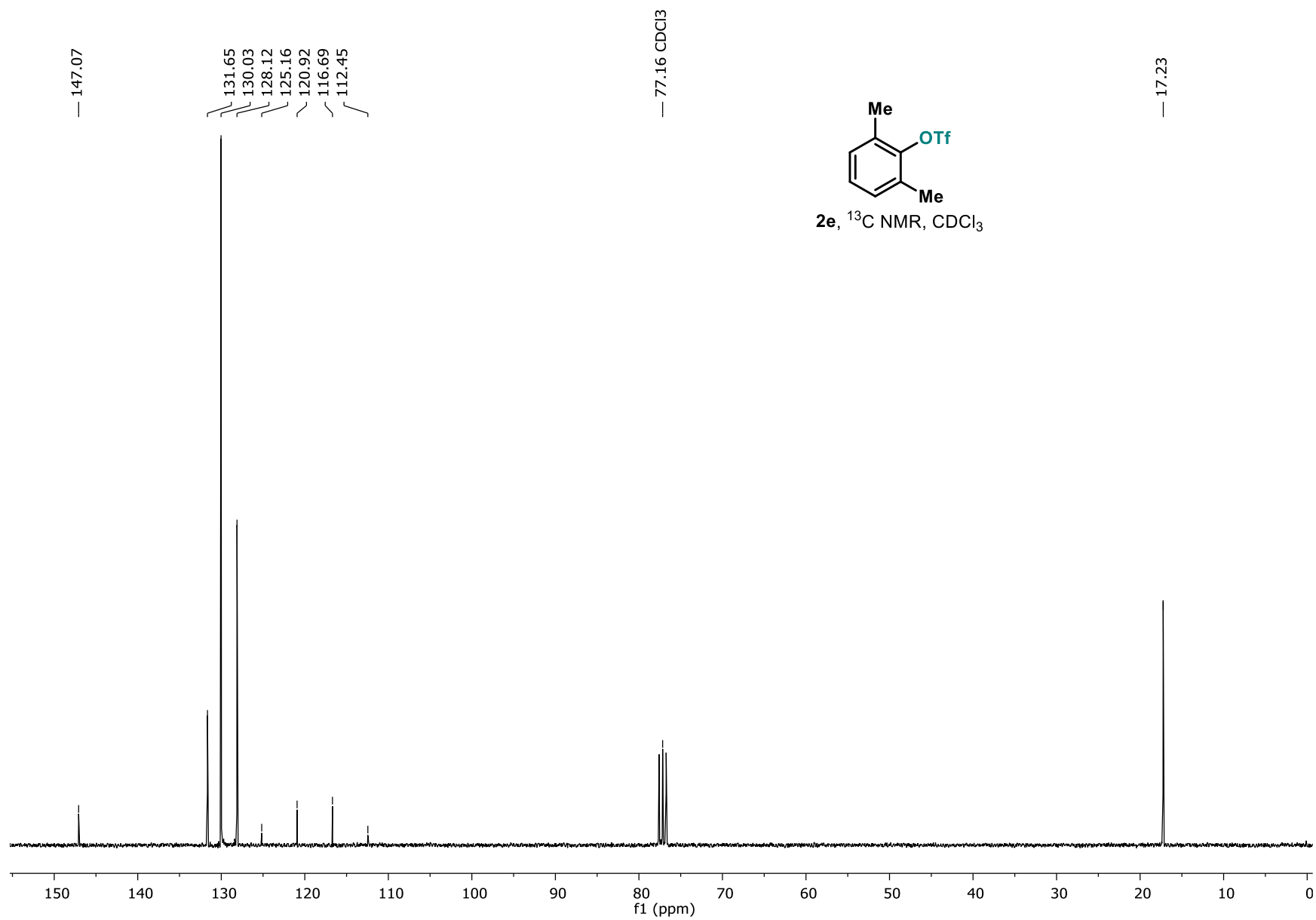


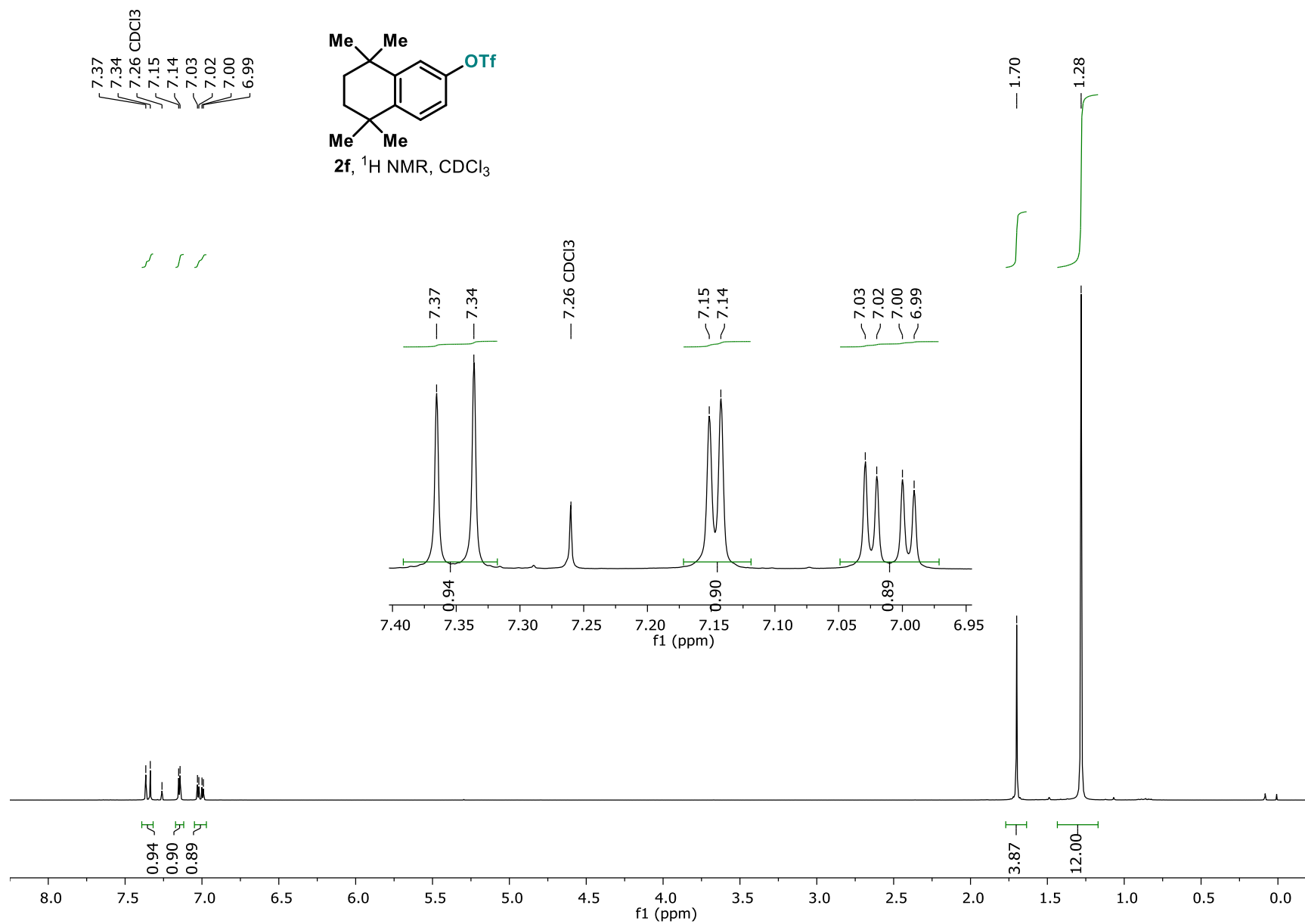


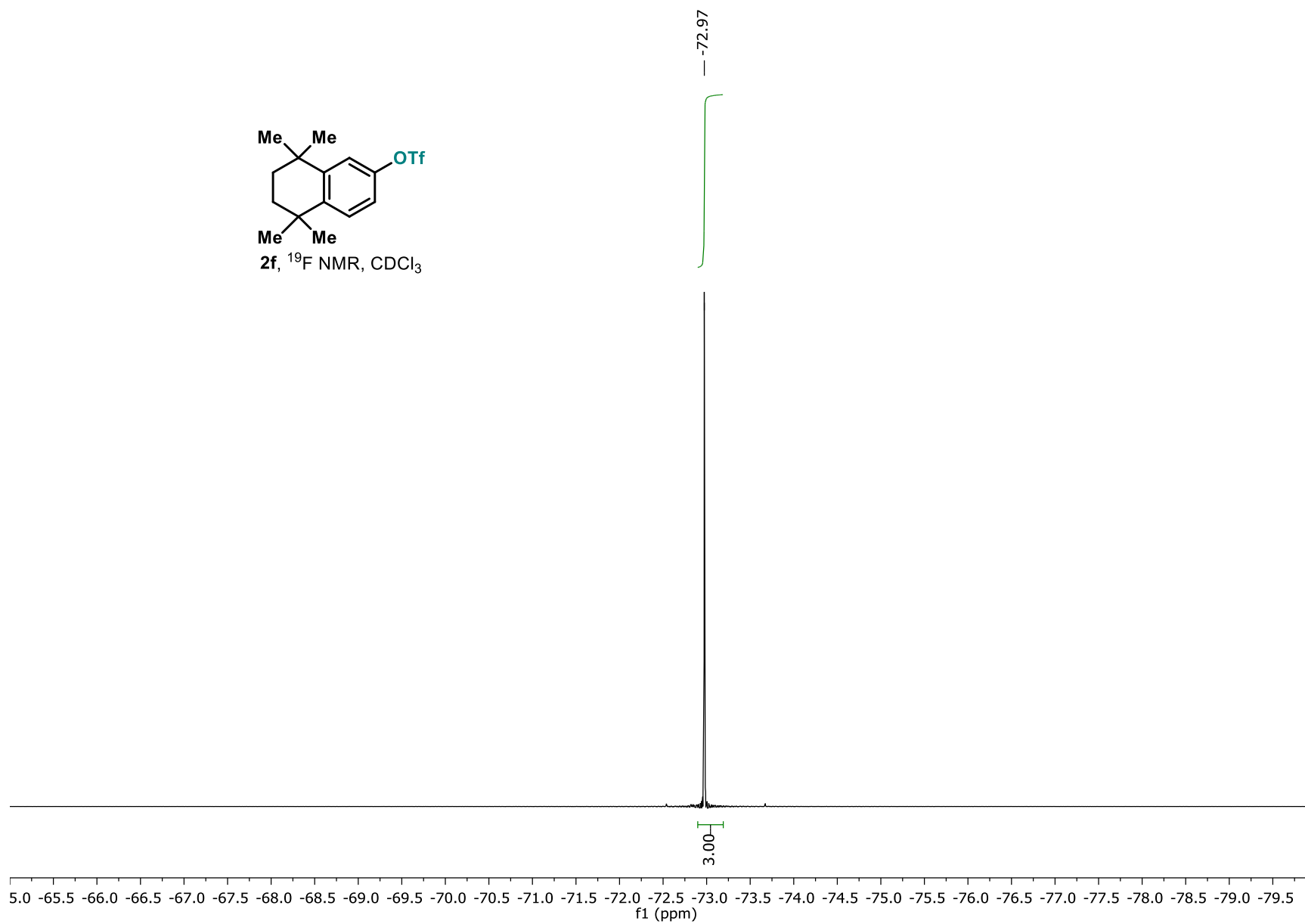
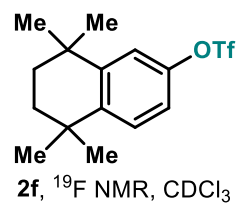


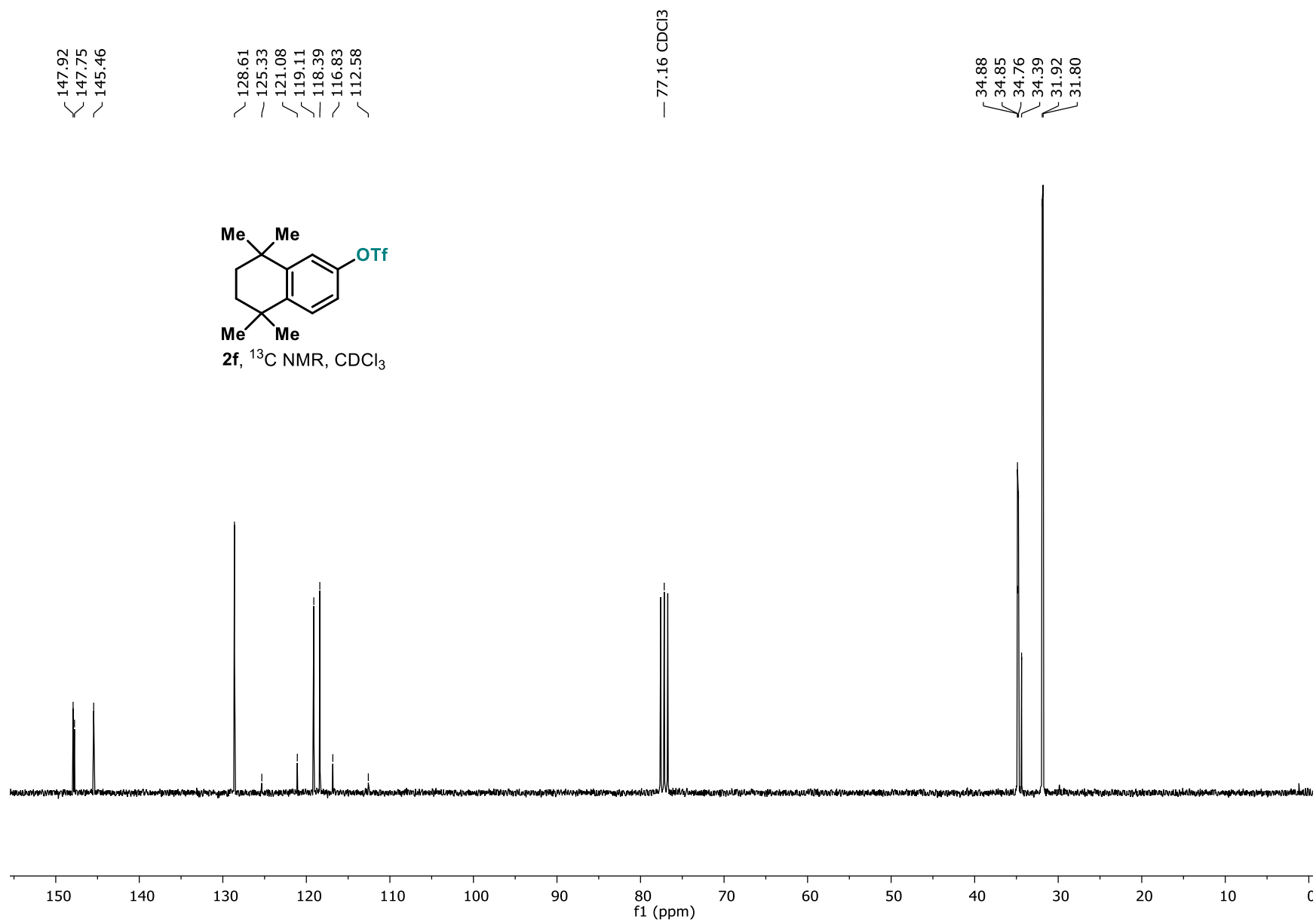


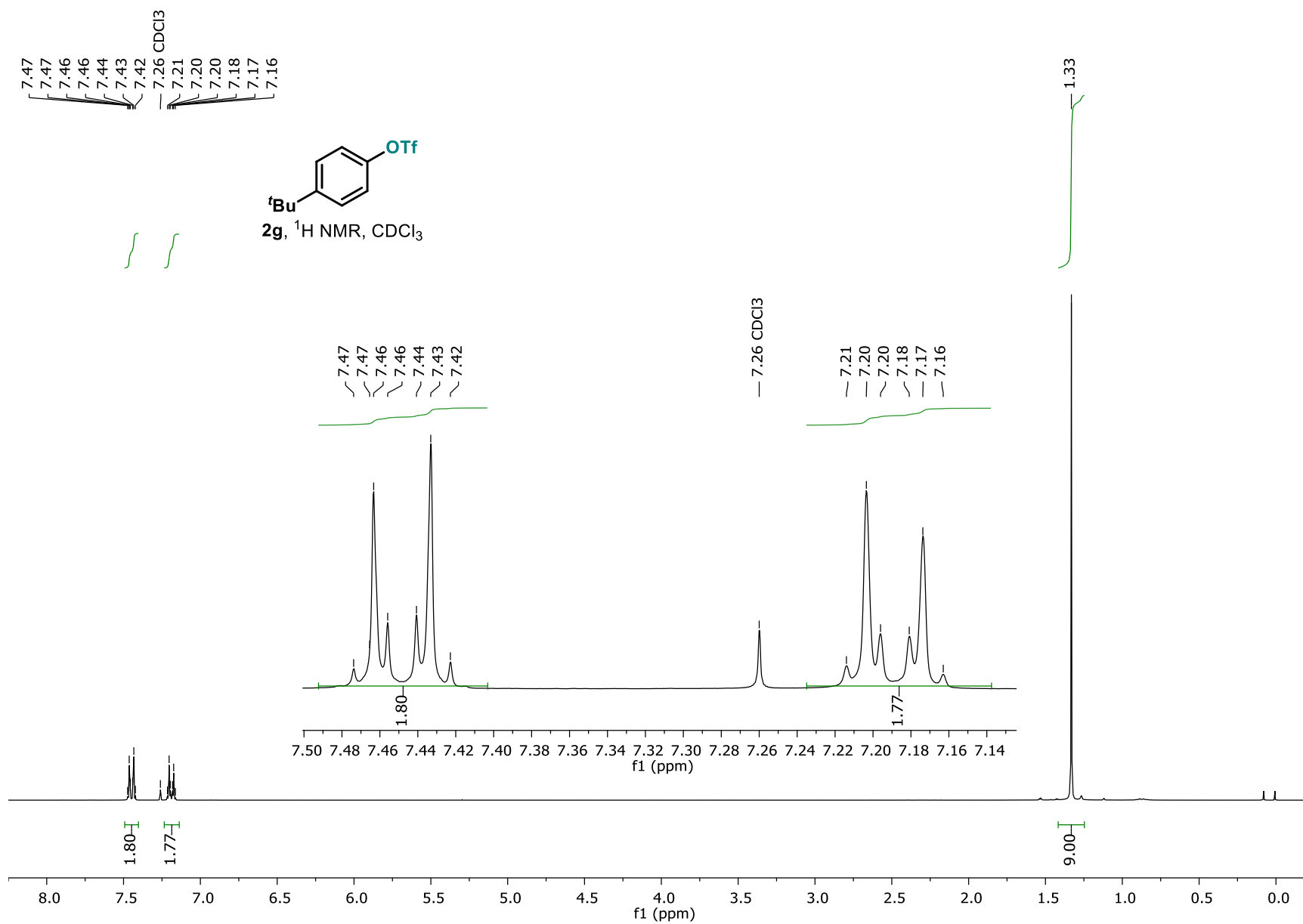
S118

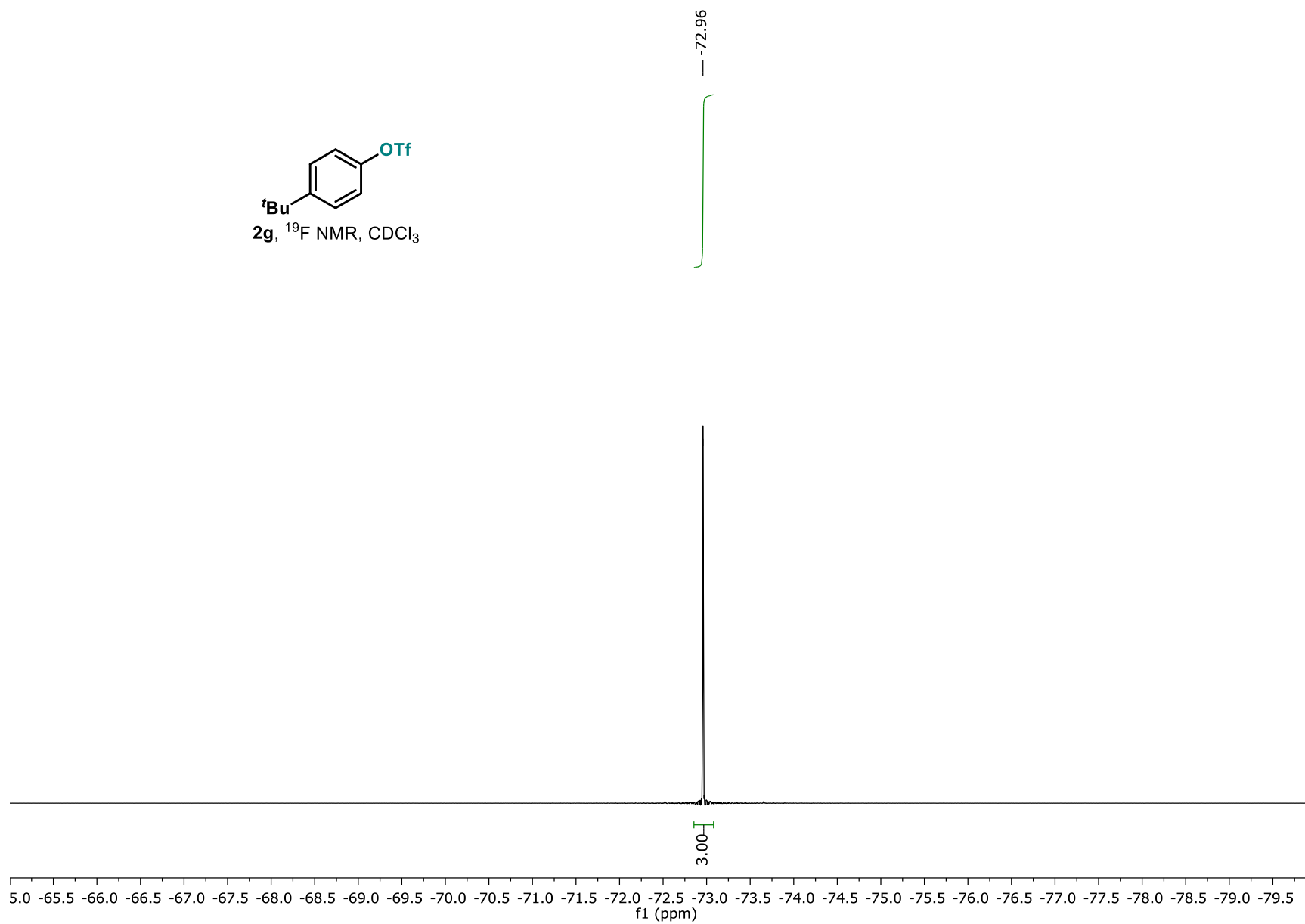
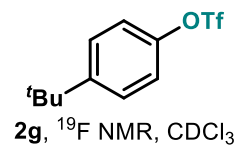




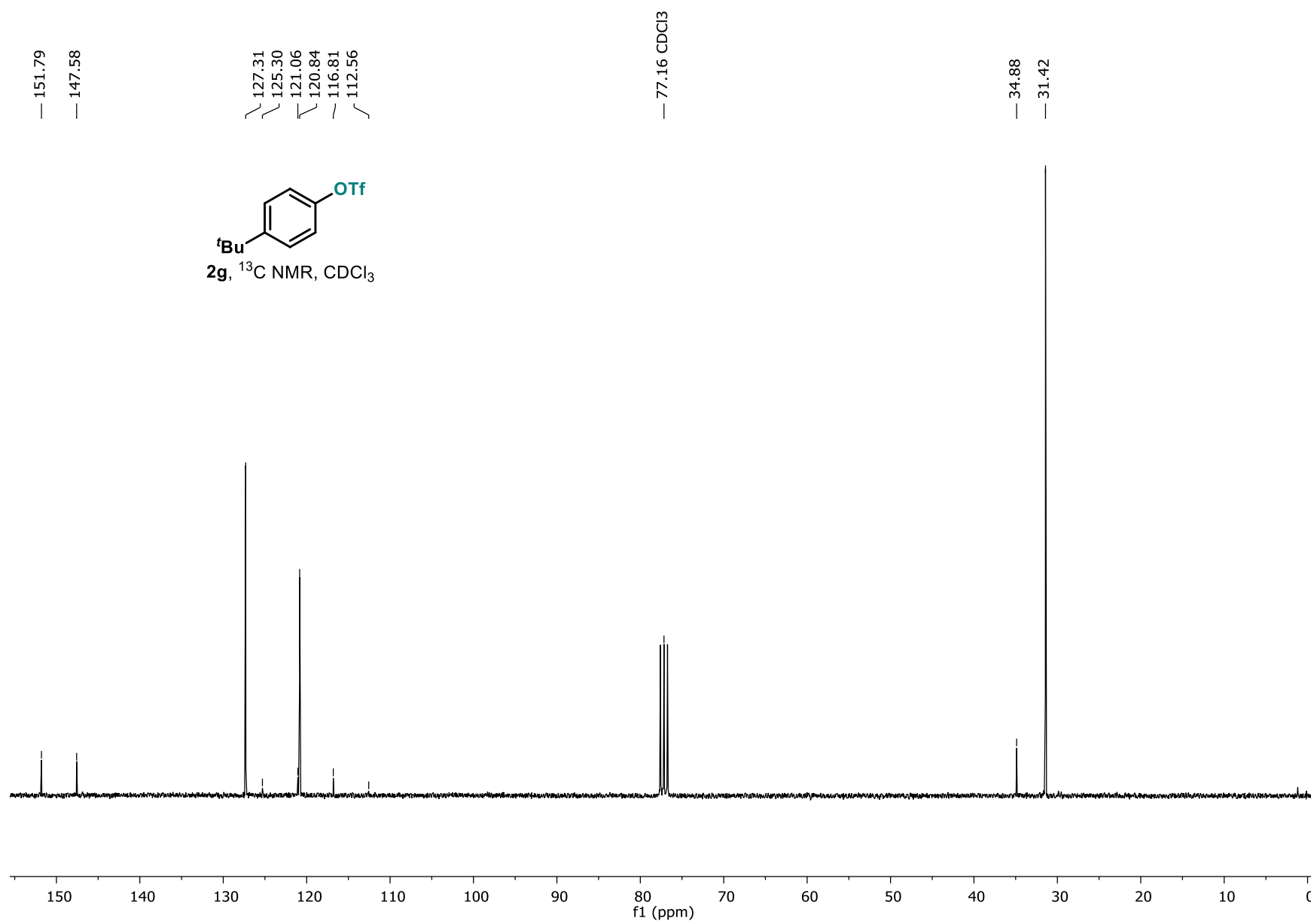


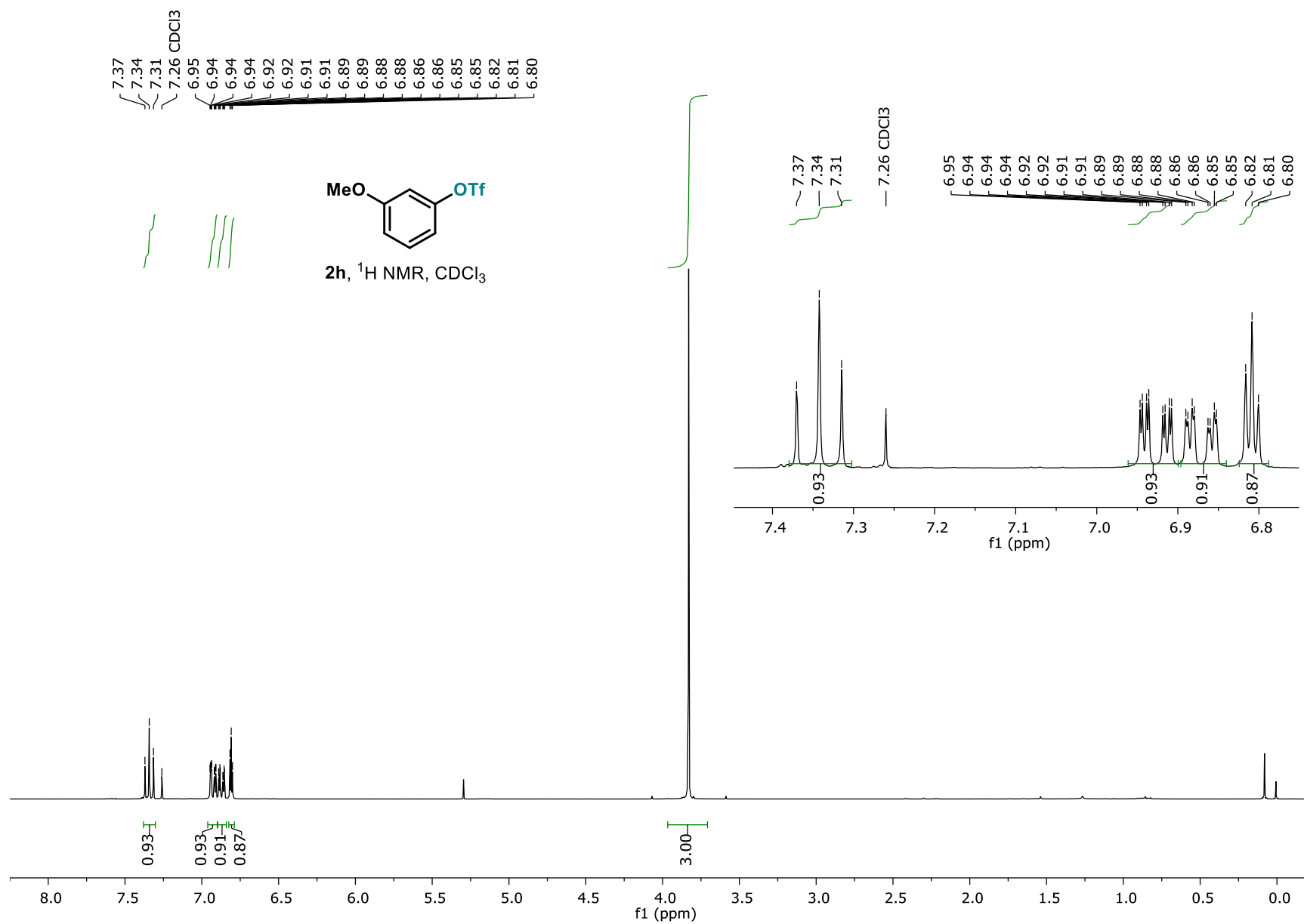


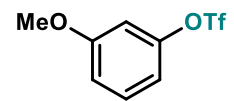




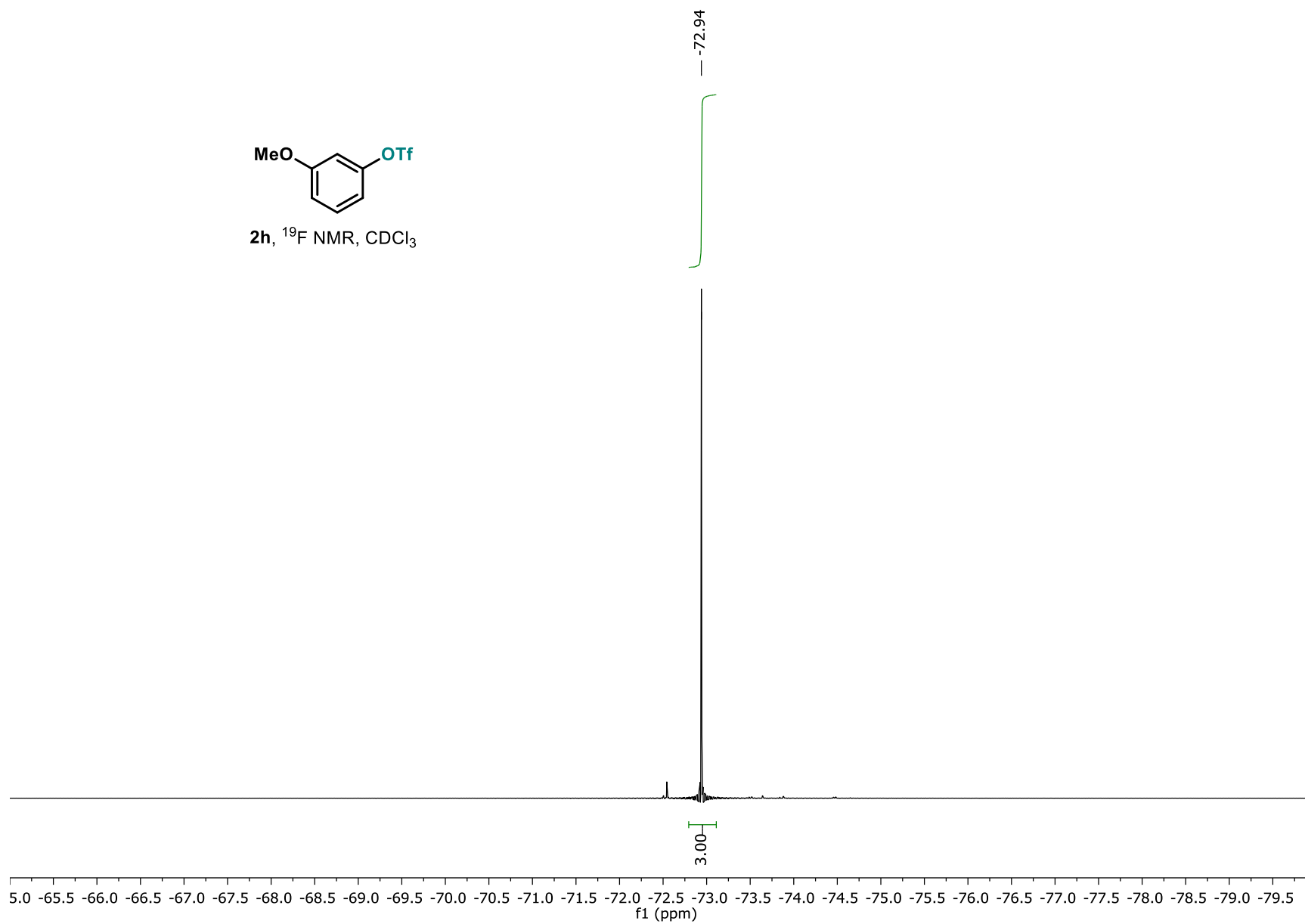


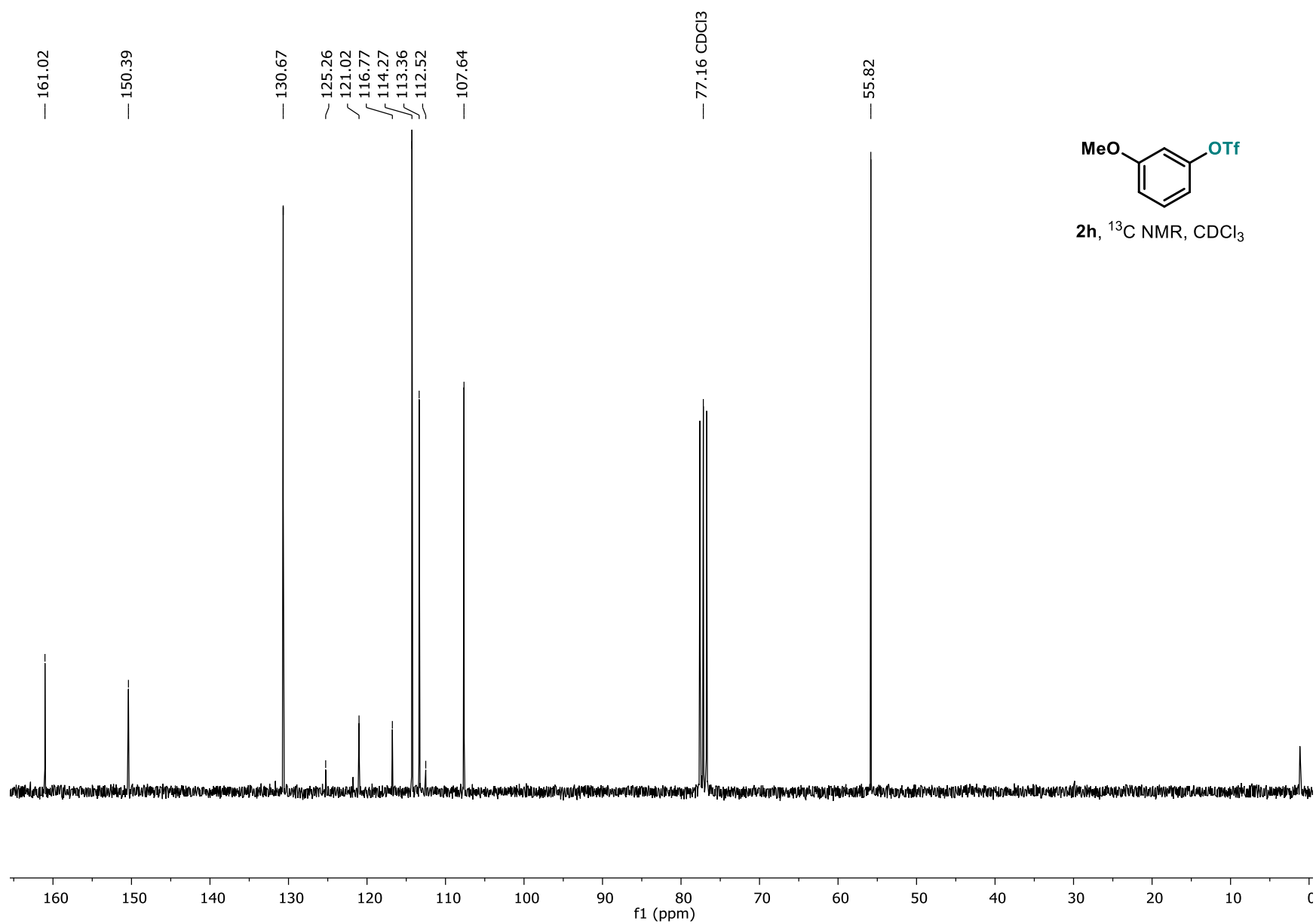


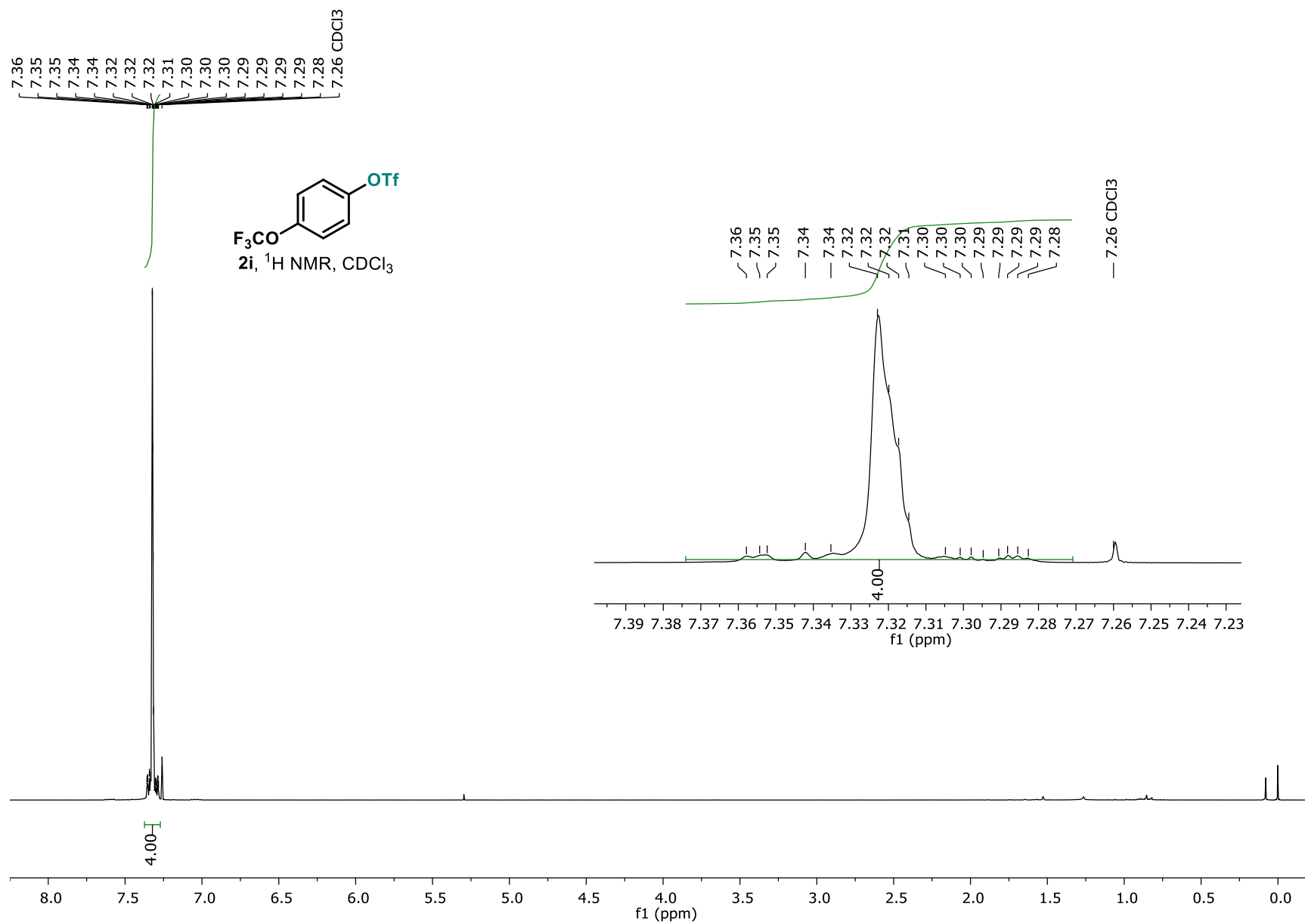


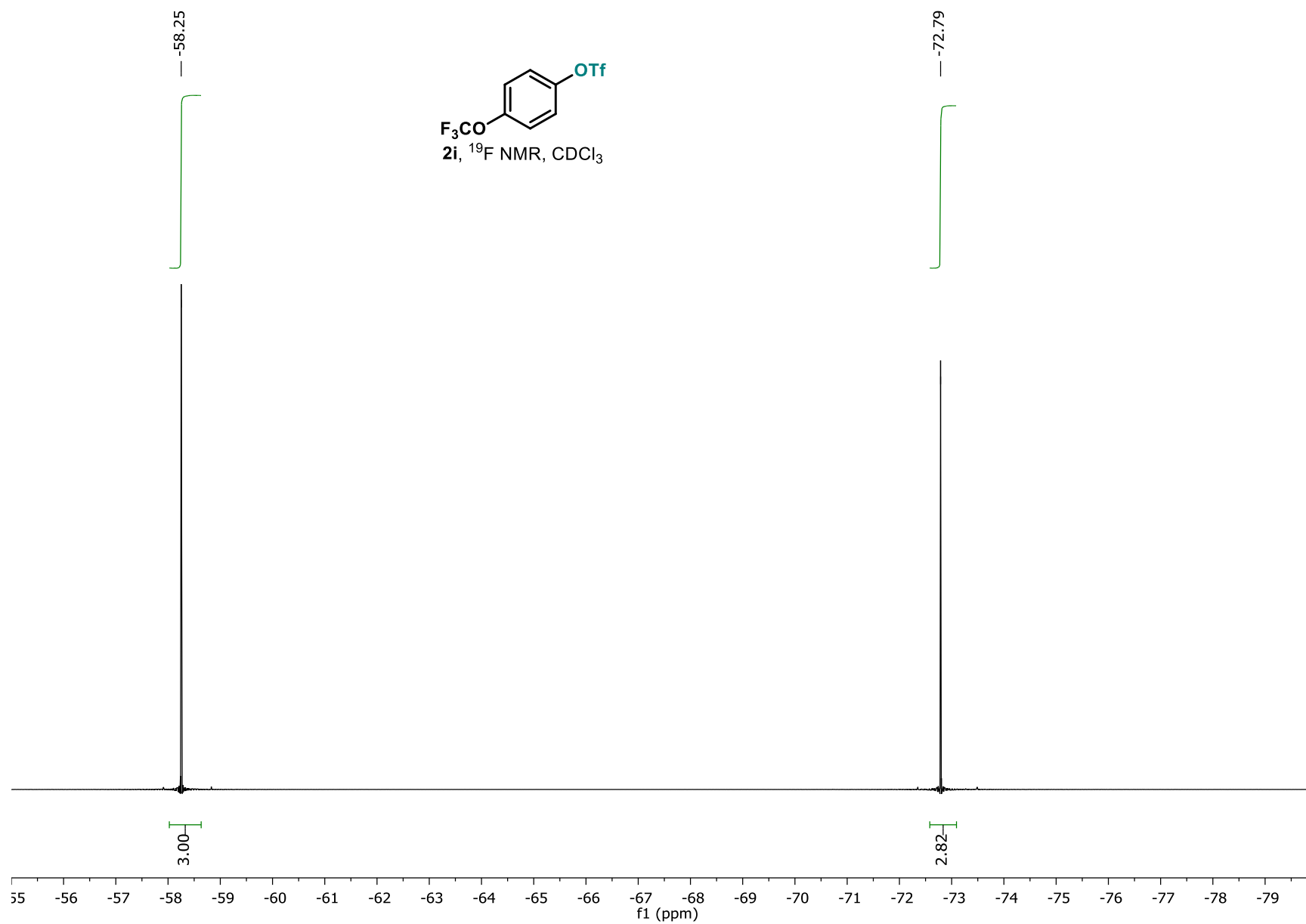


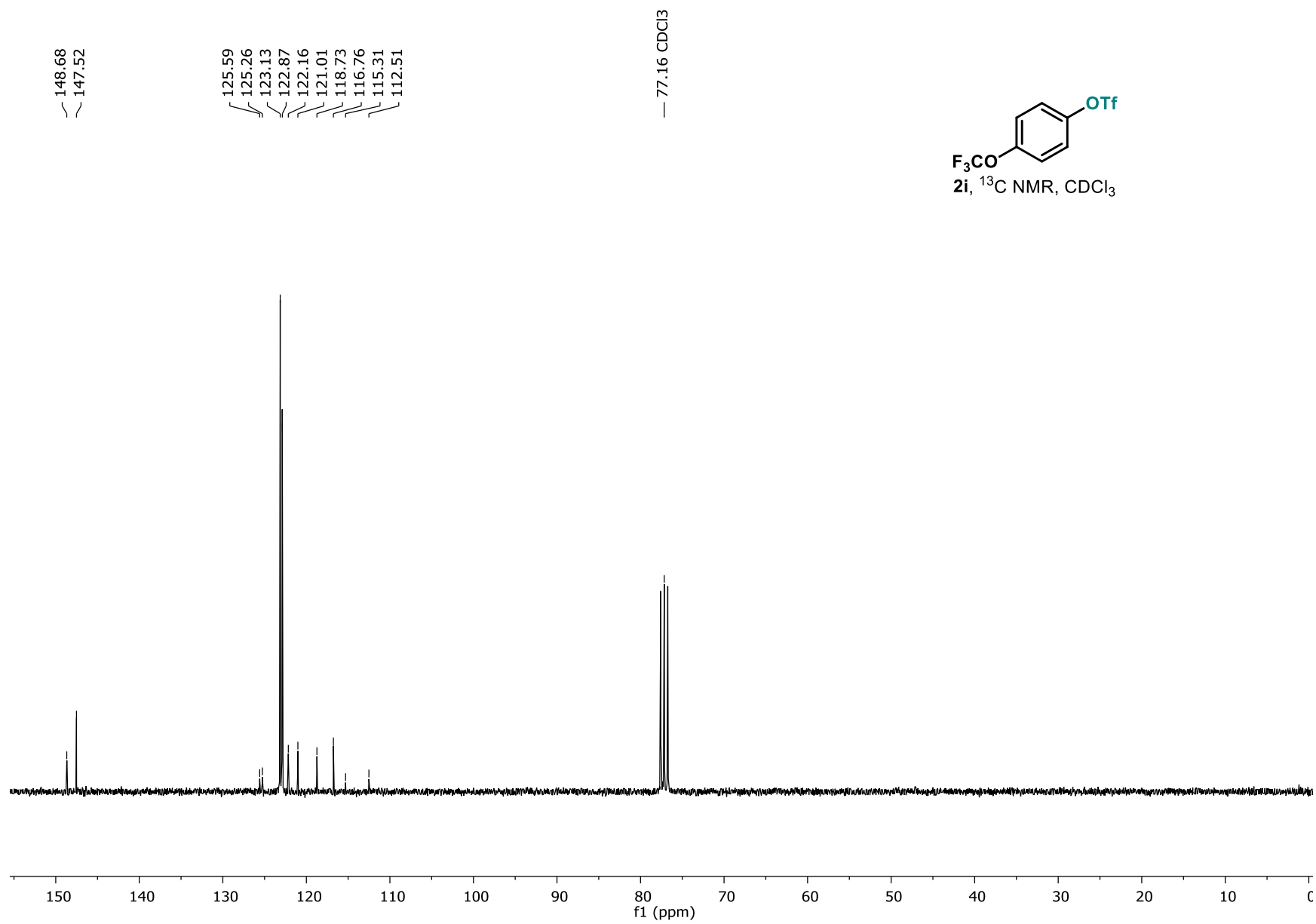
2h,  $^{19}\text{F}$  NMR,  $\text{CDCl}_3$

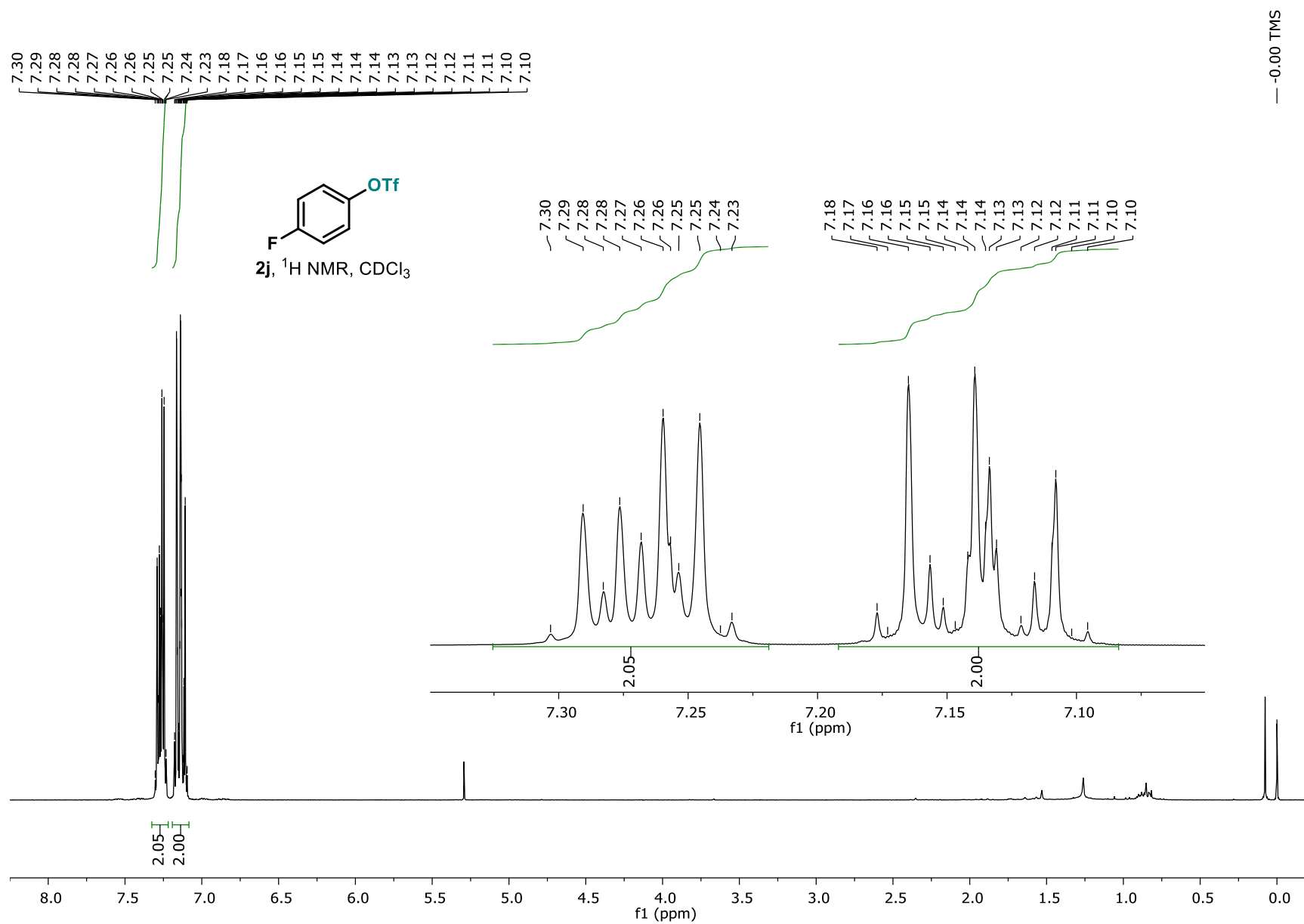




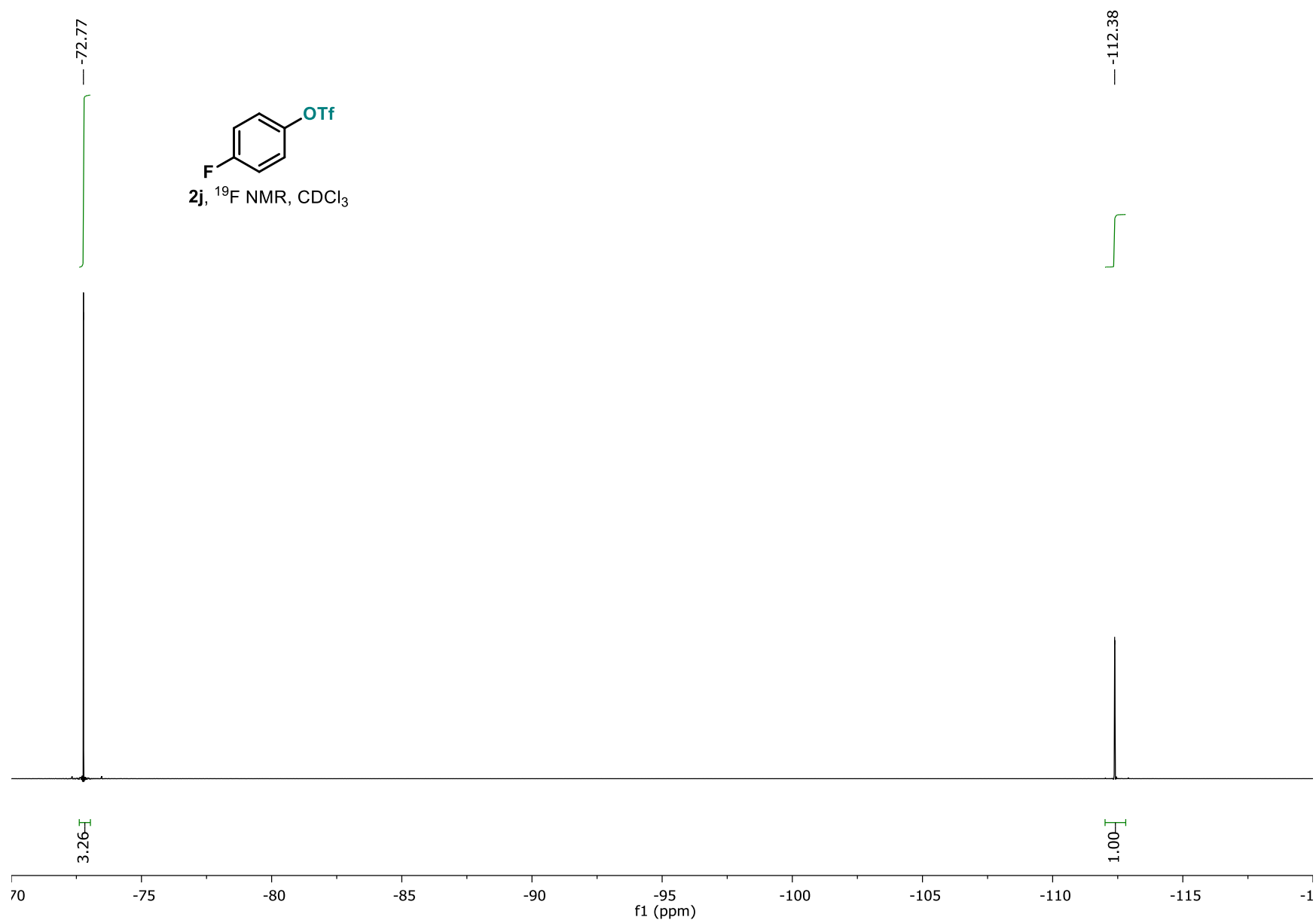


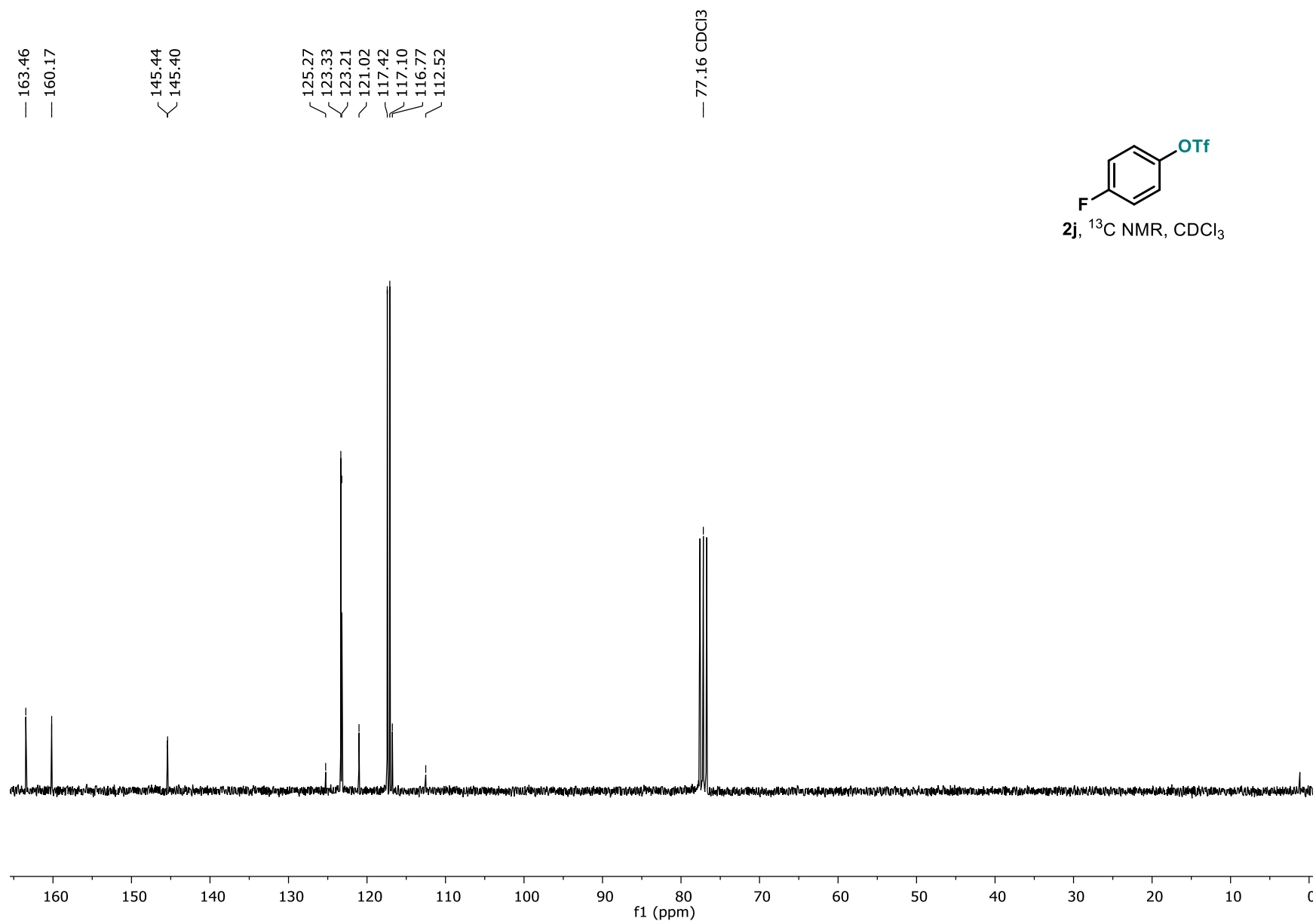


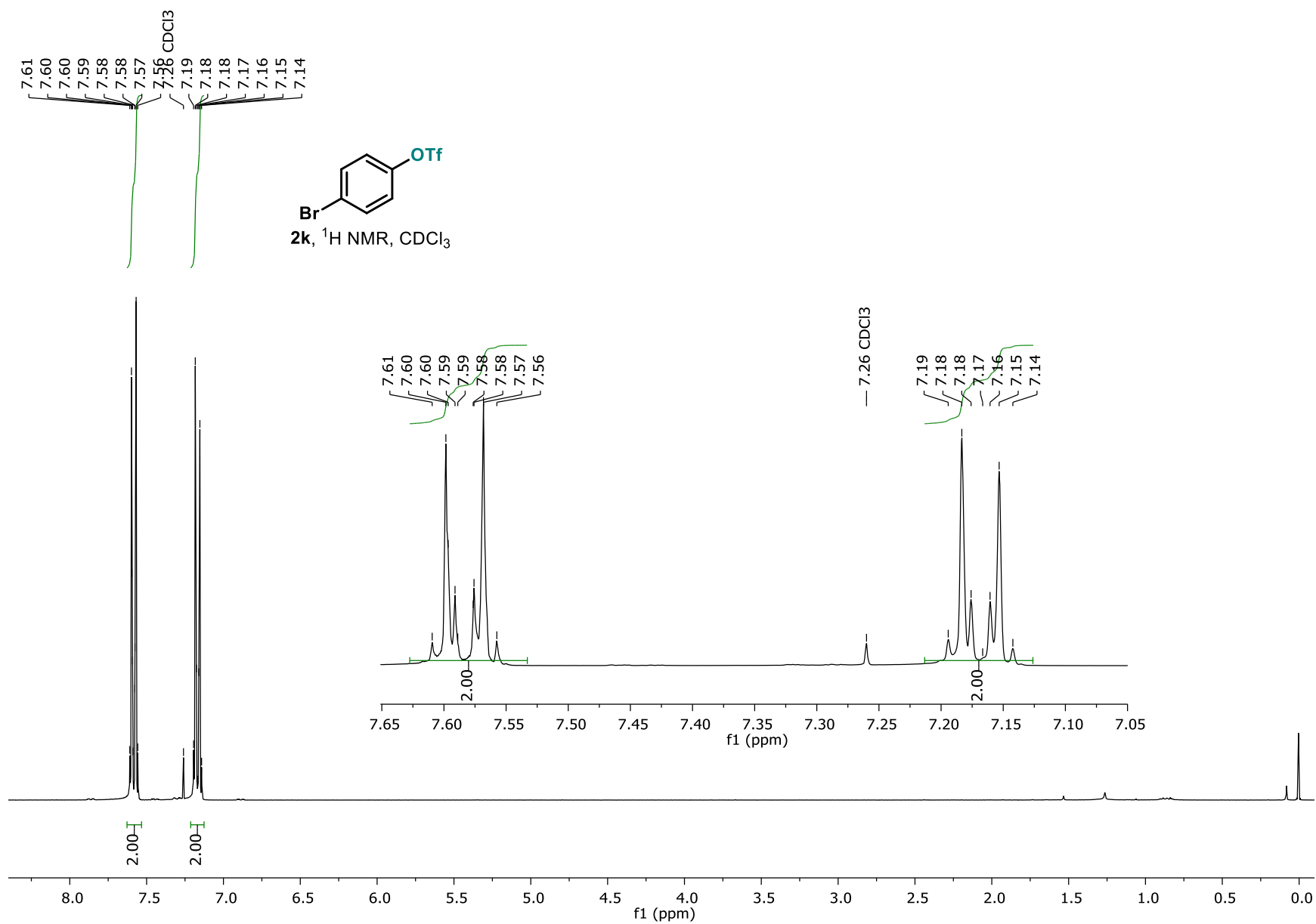


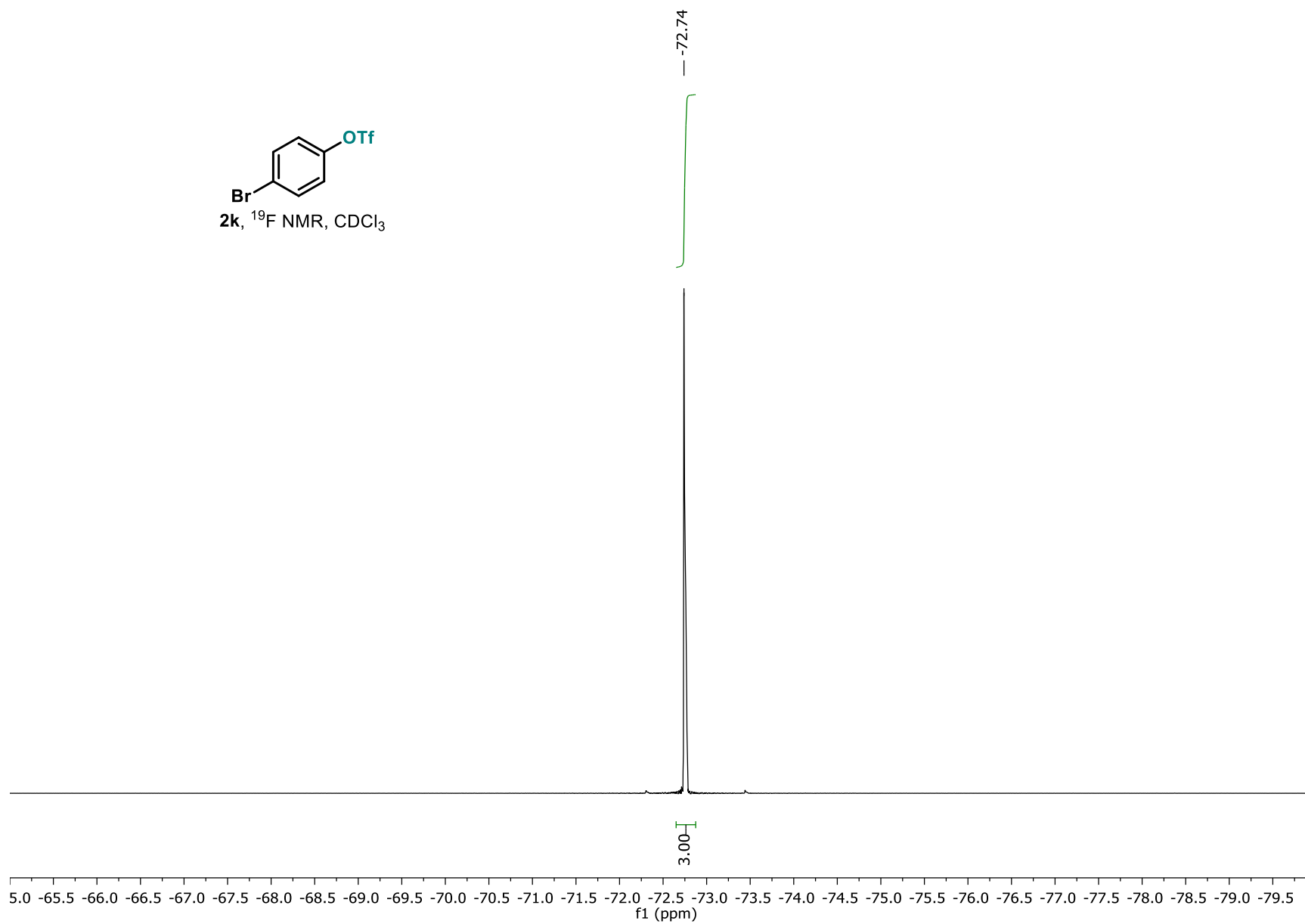
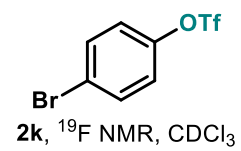


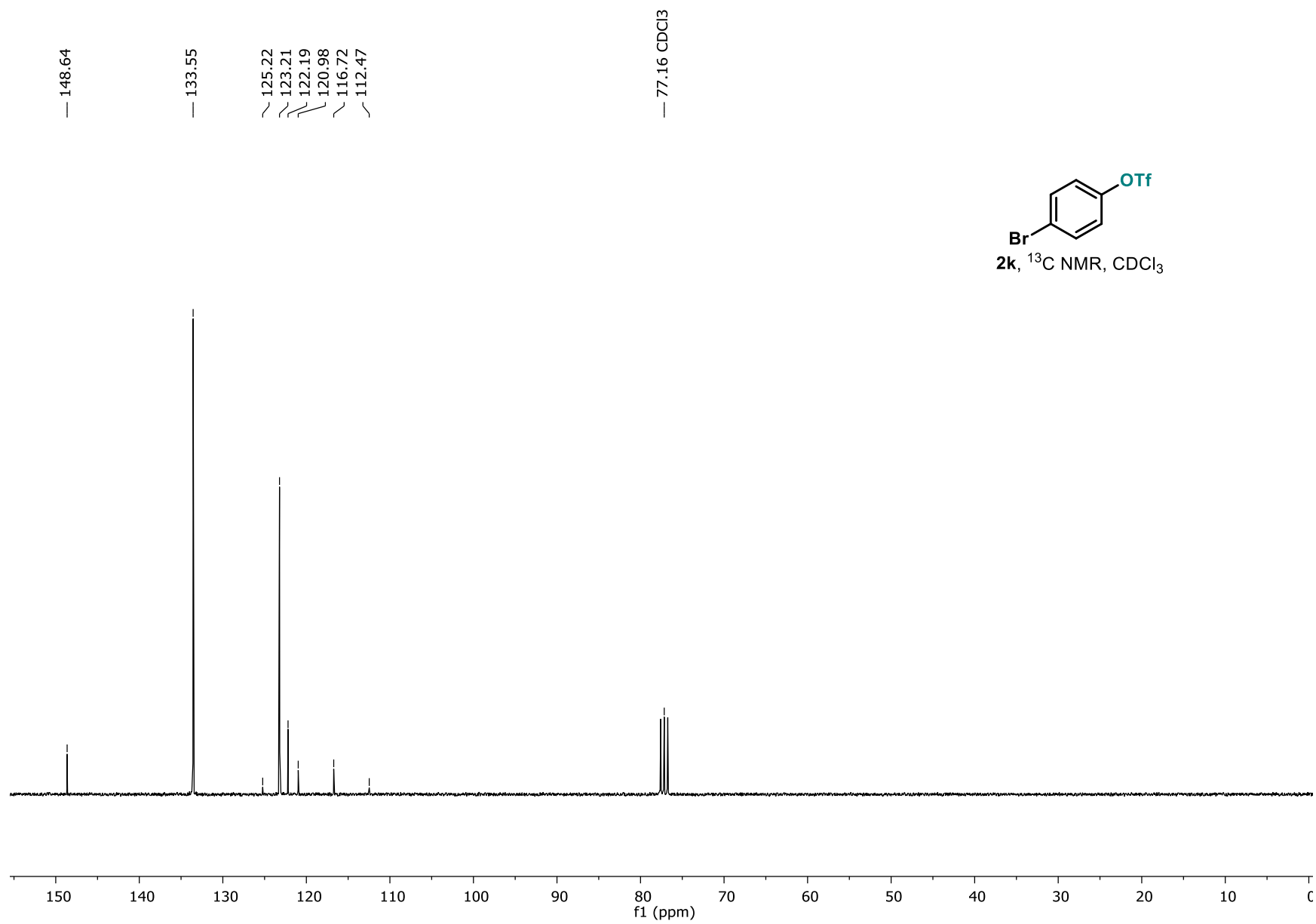


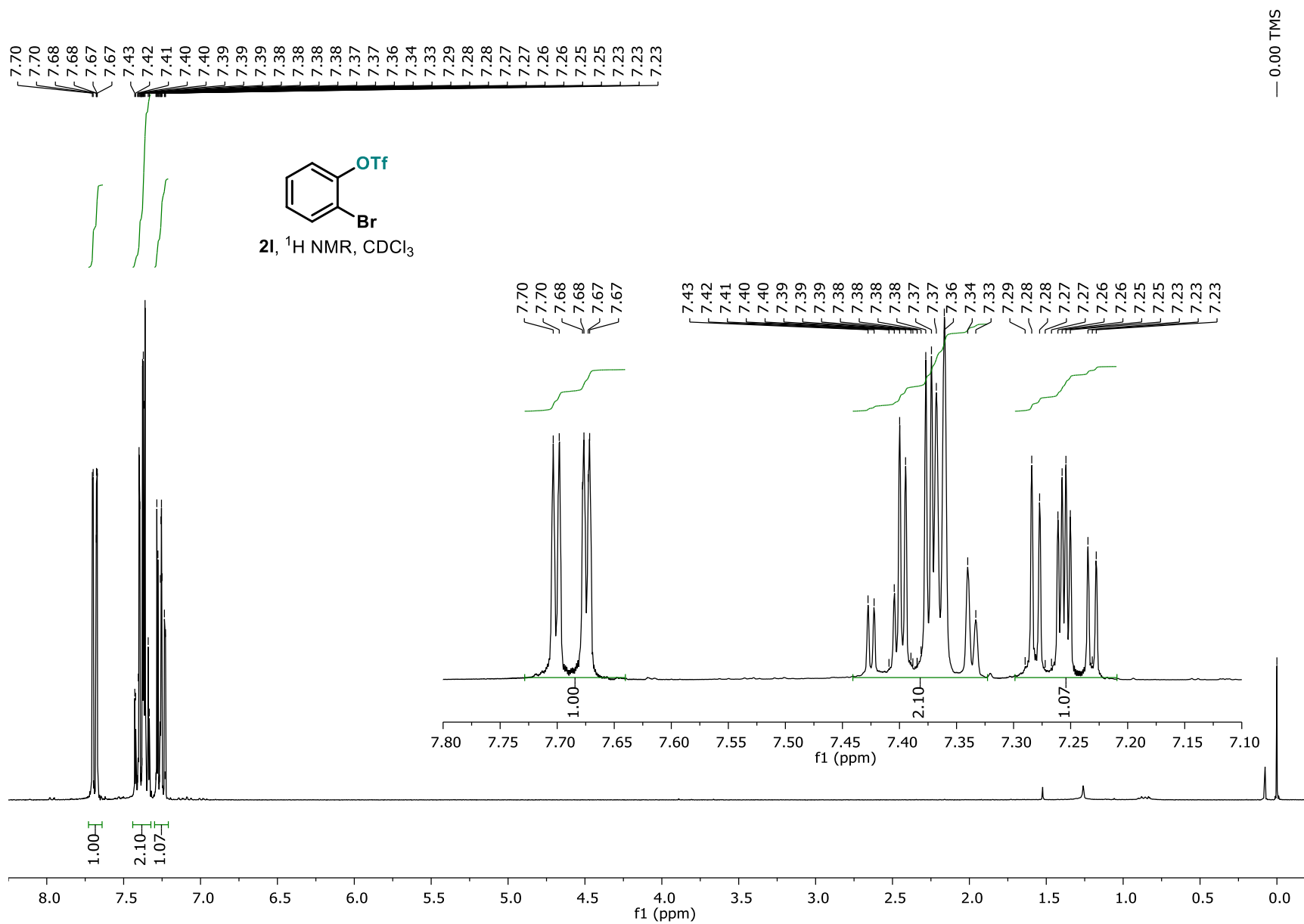


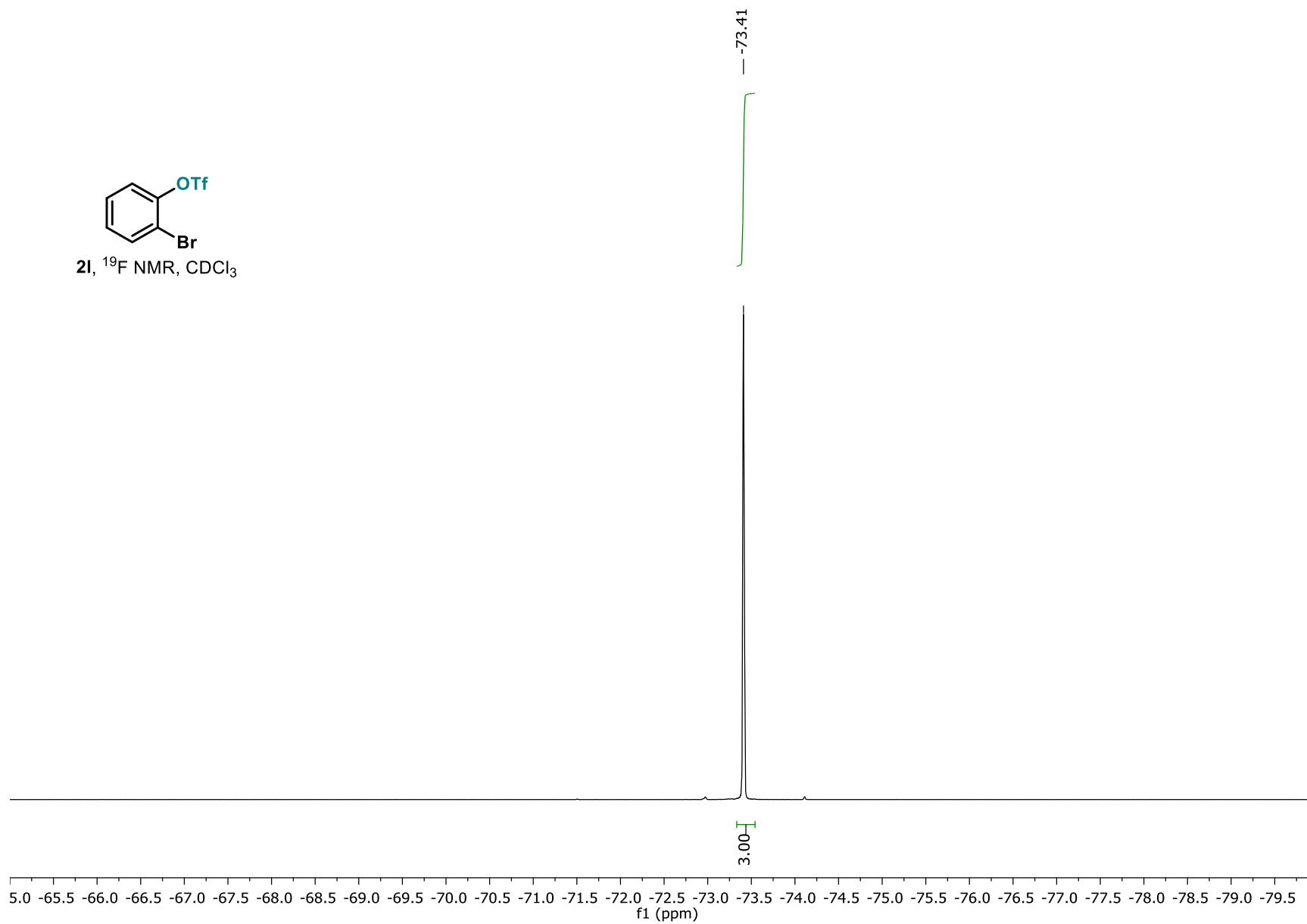
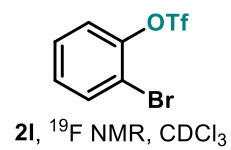




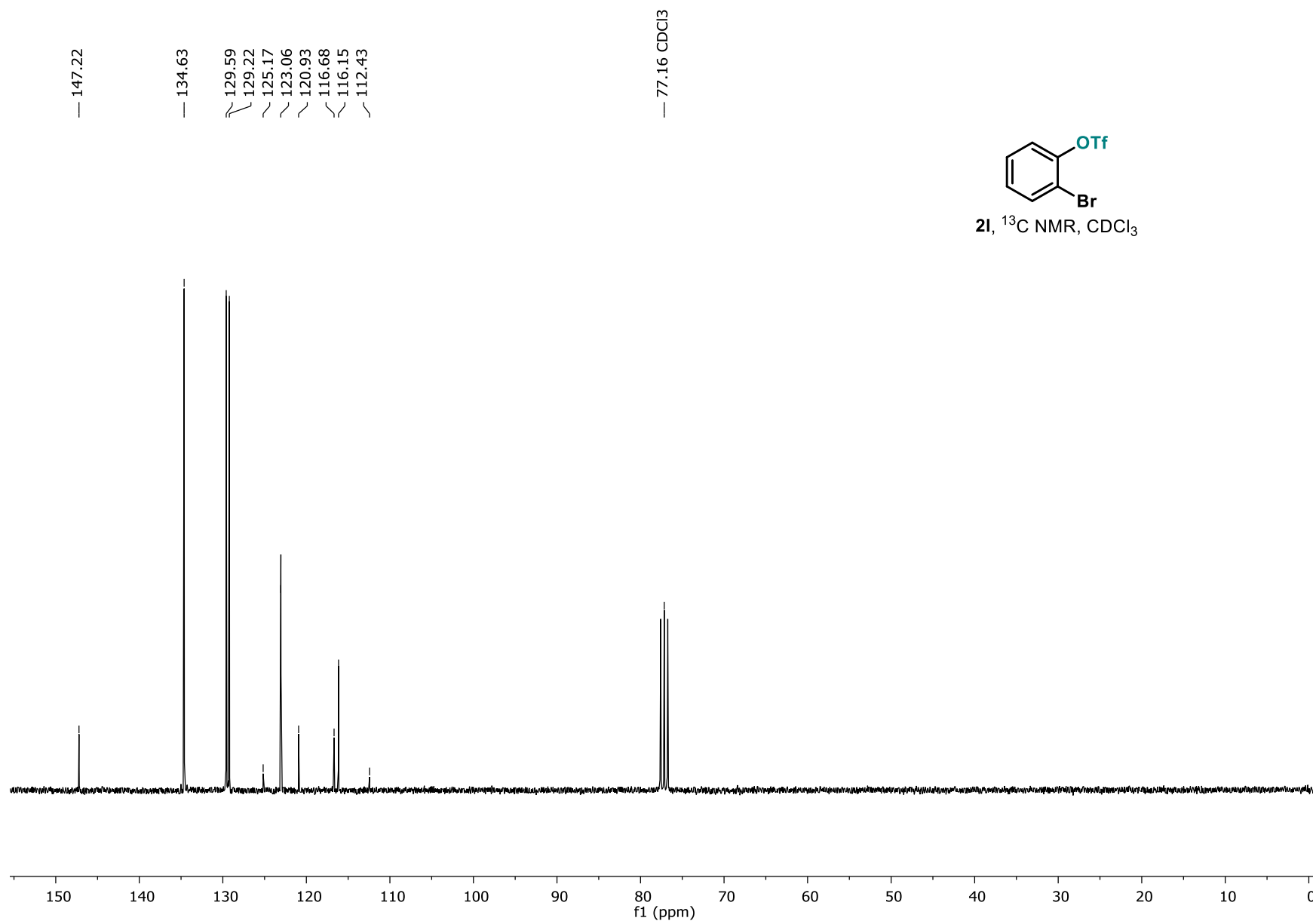




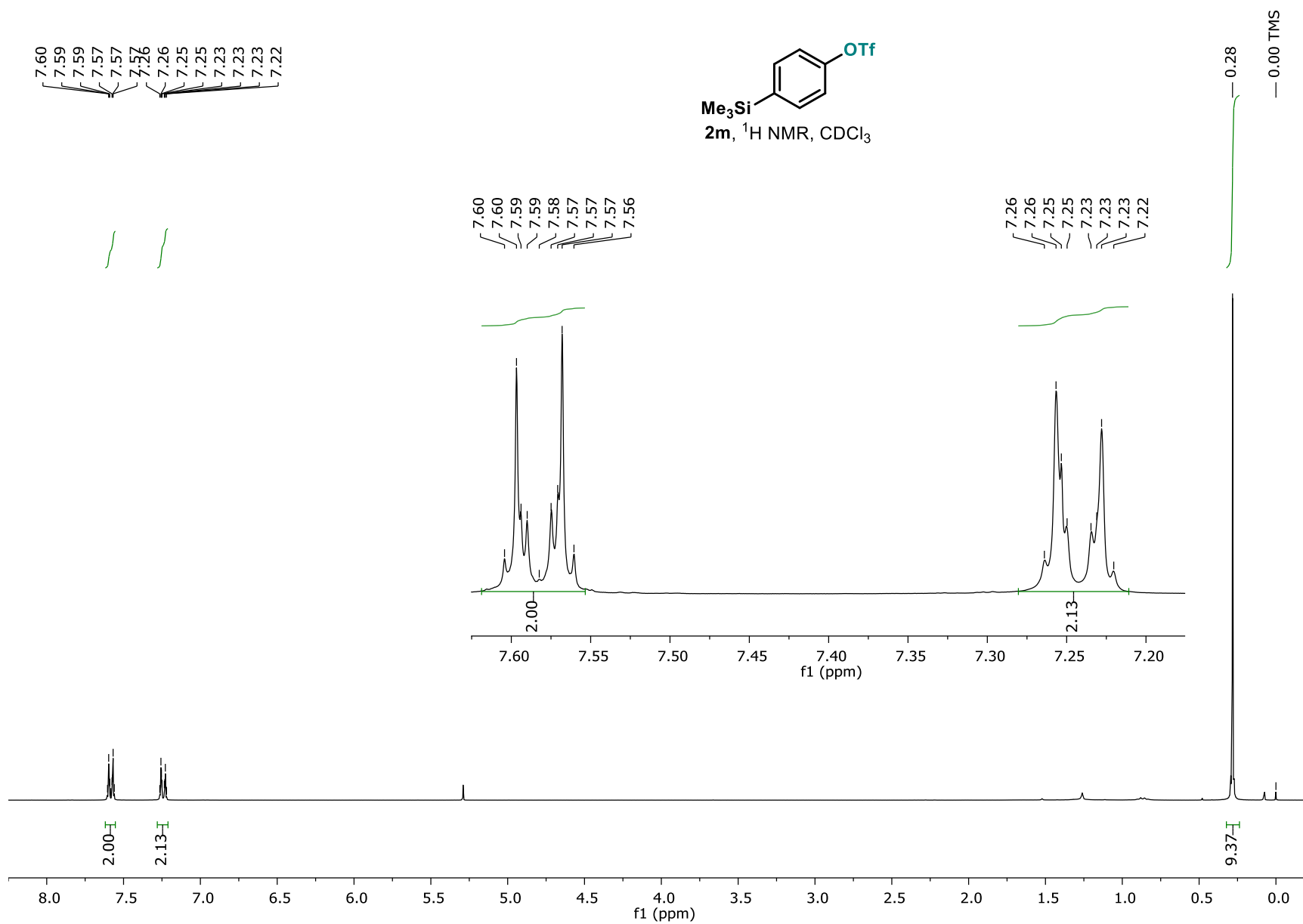


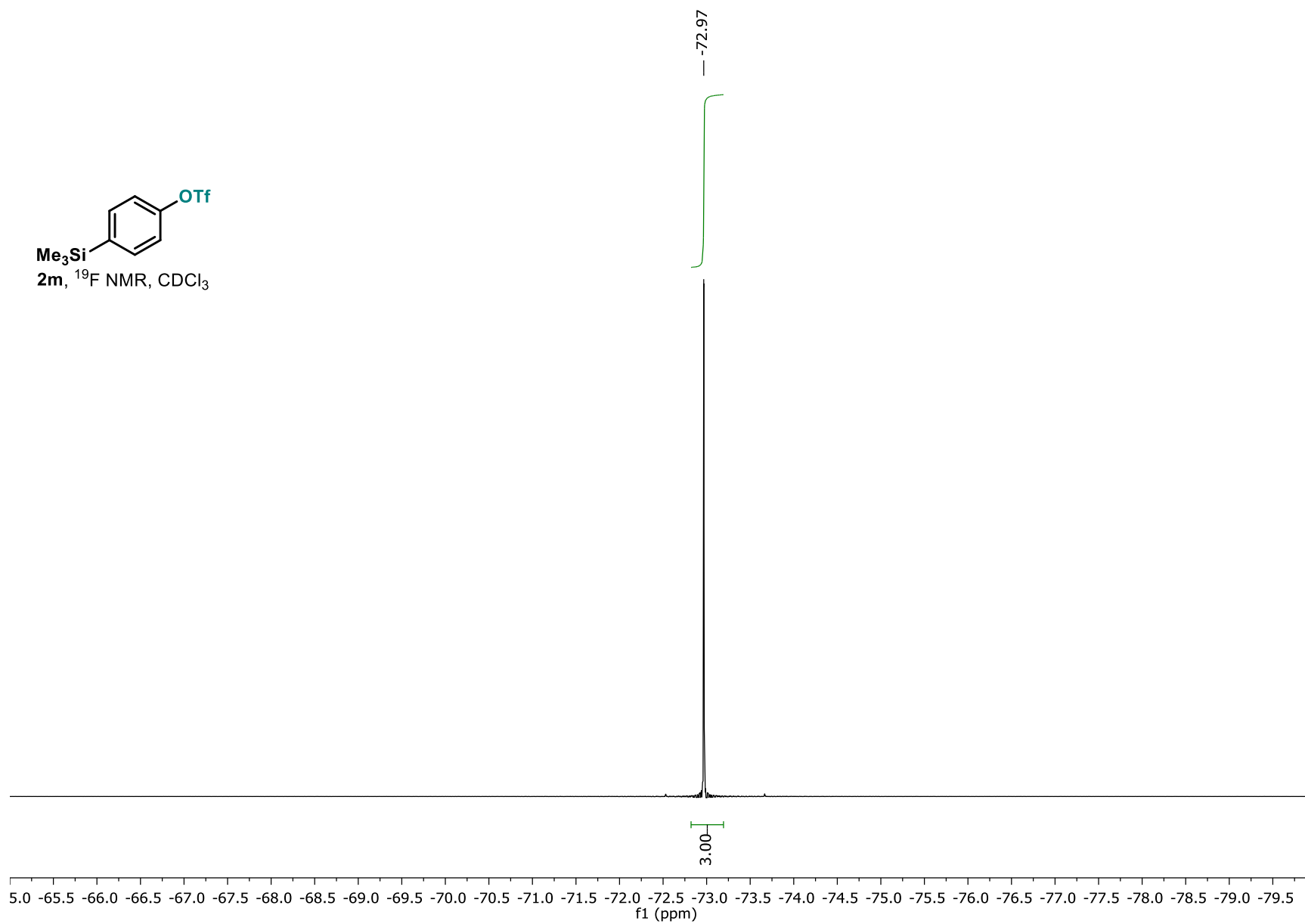
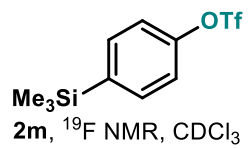


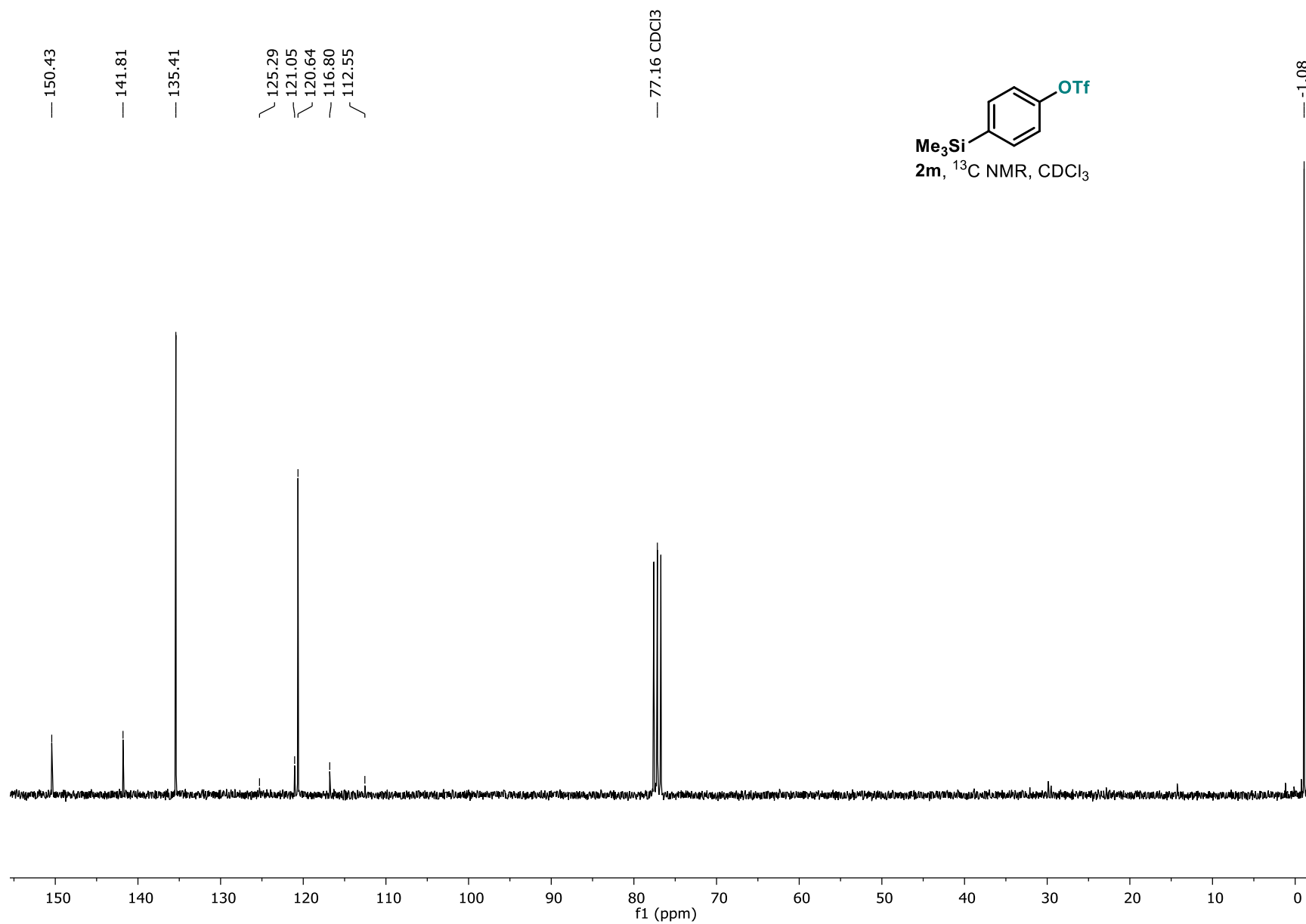
S139





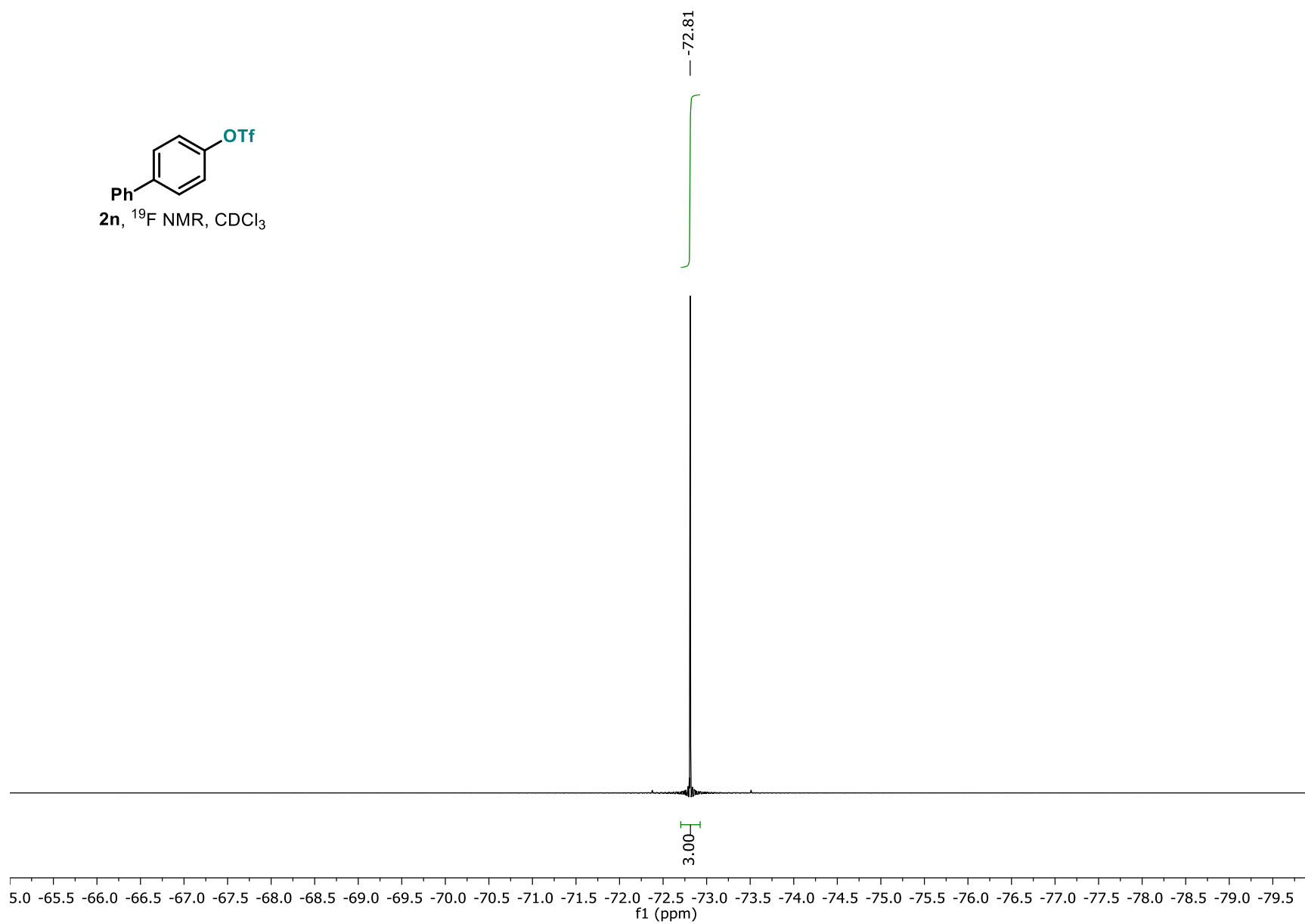
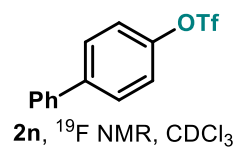


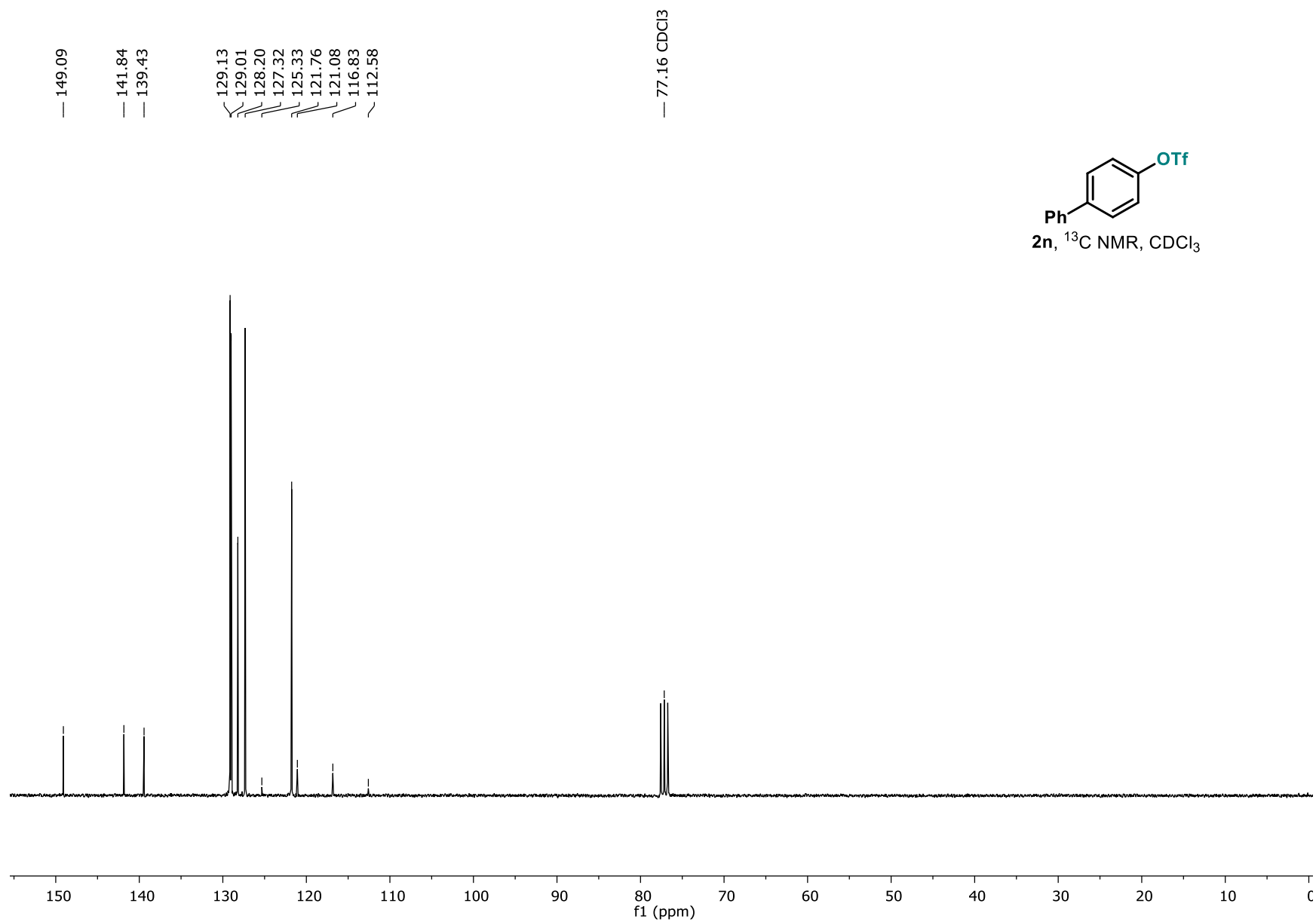


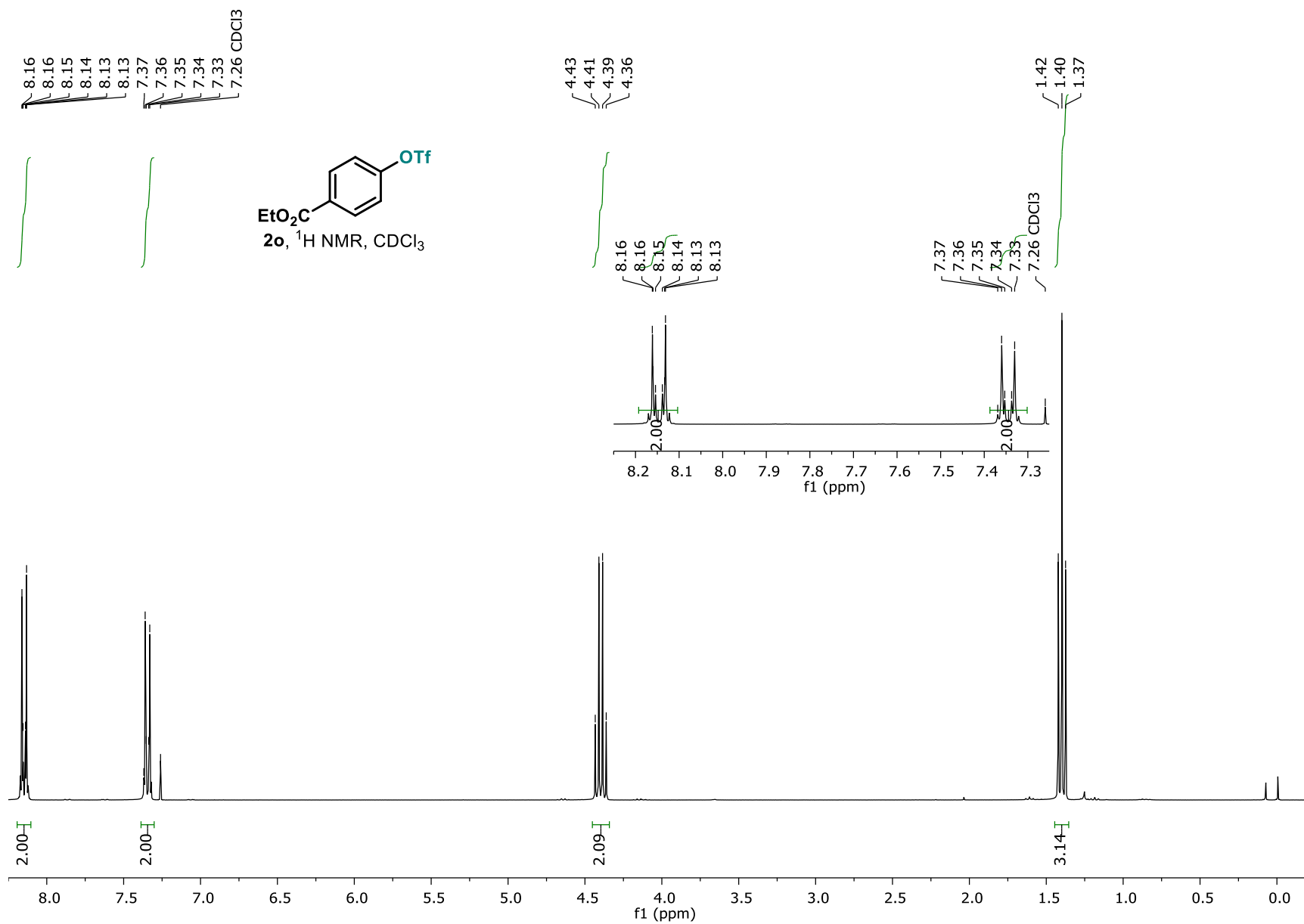


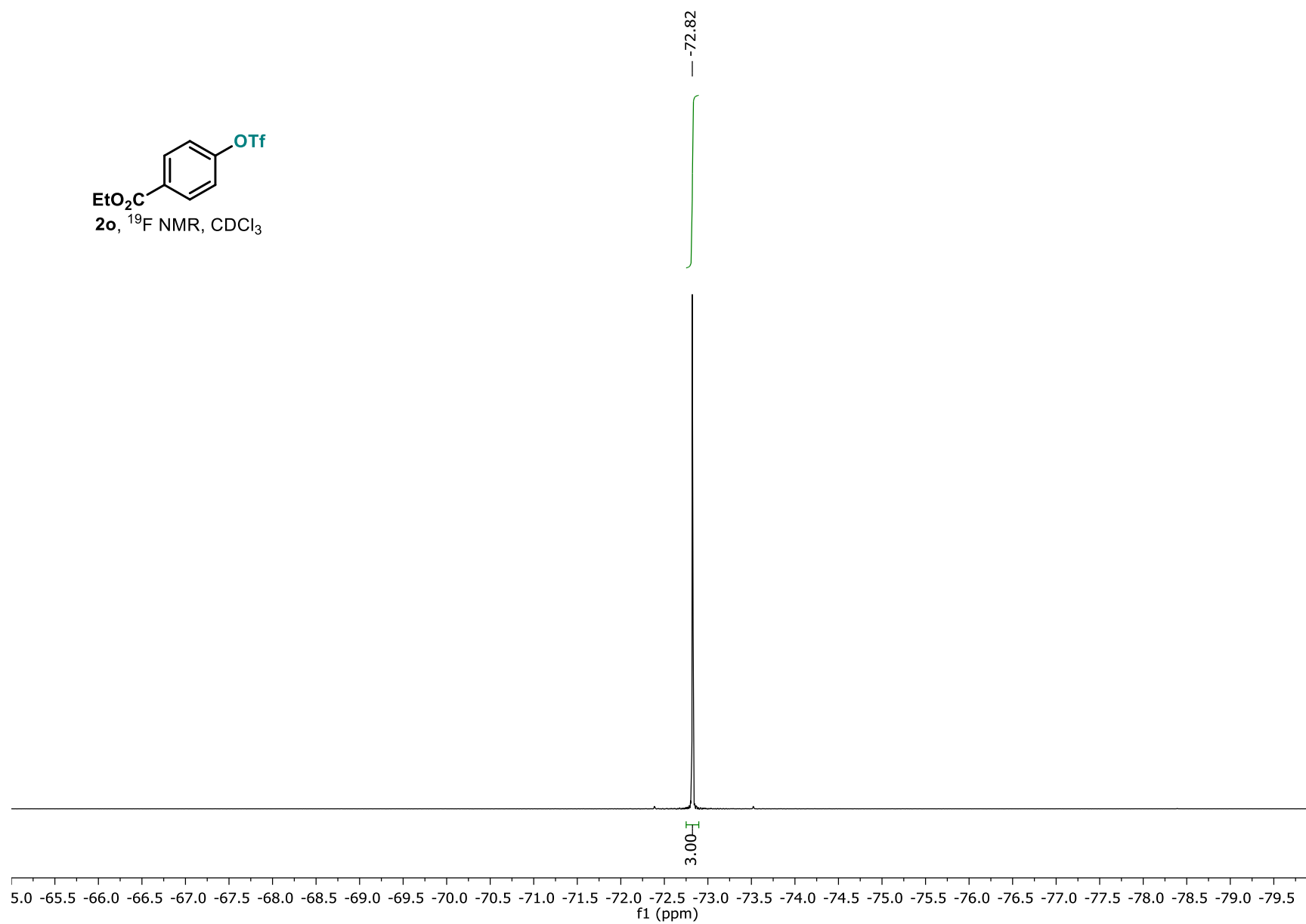
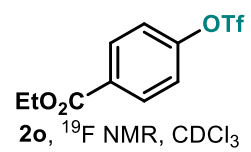
S143



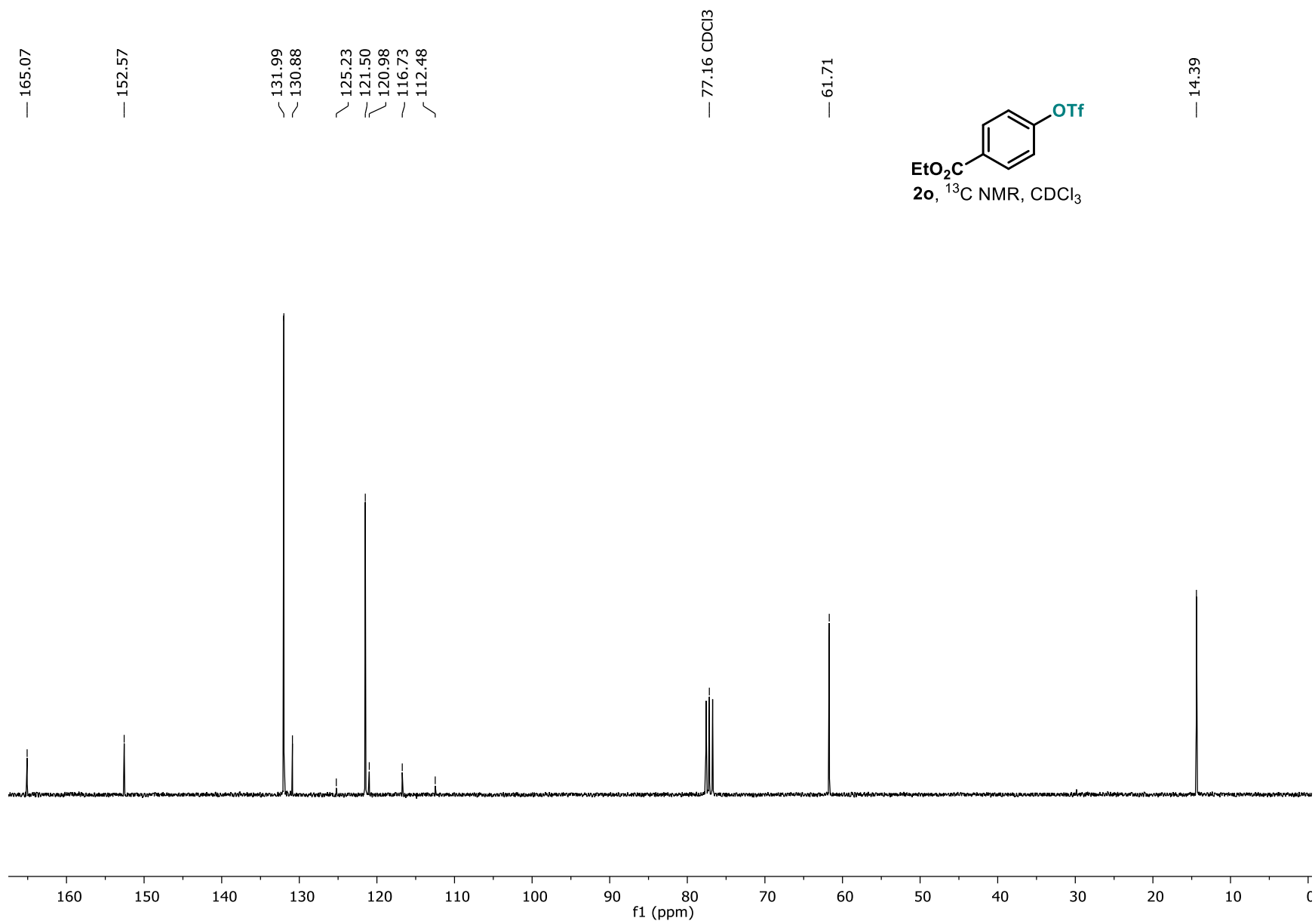


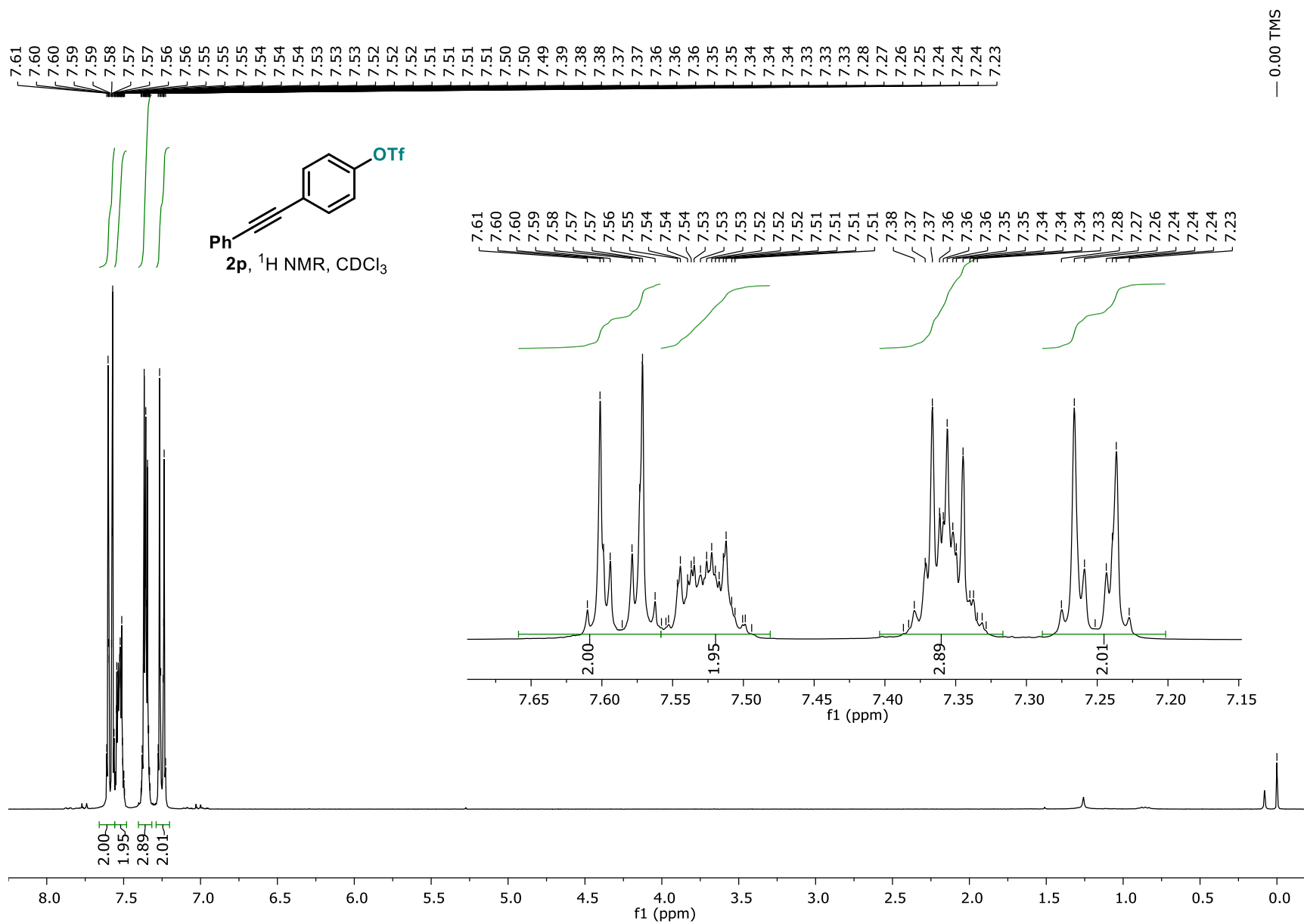


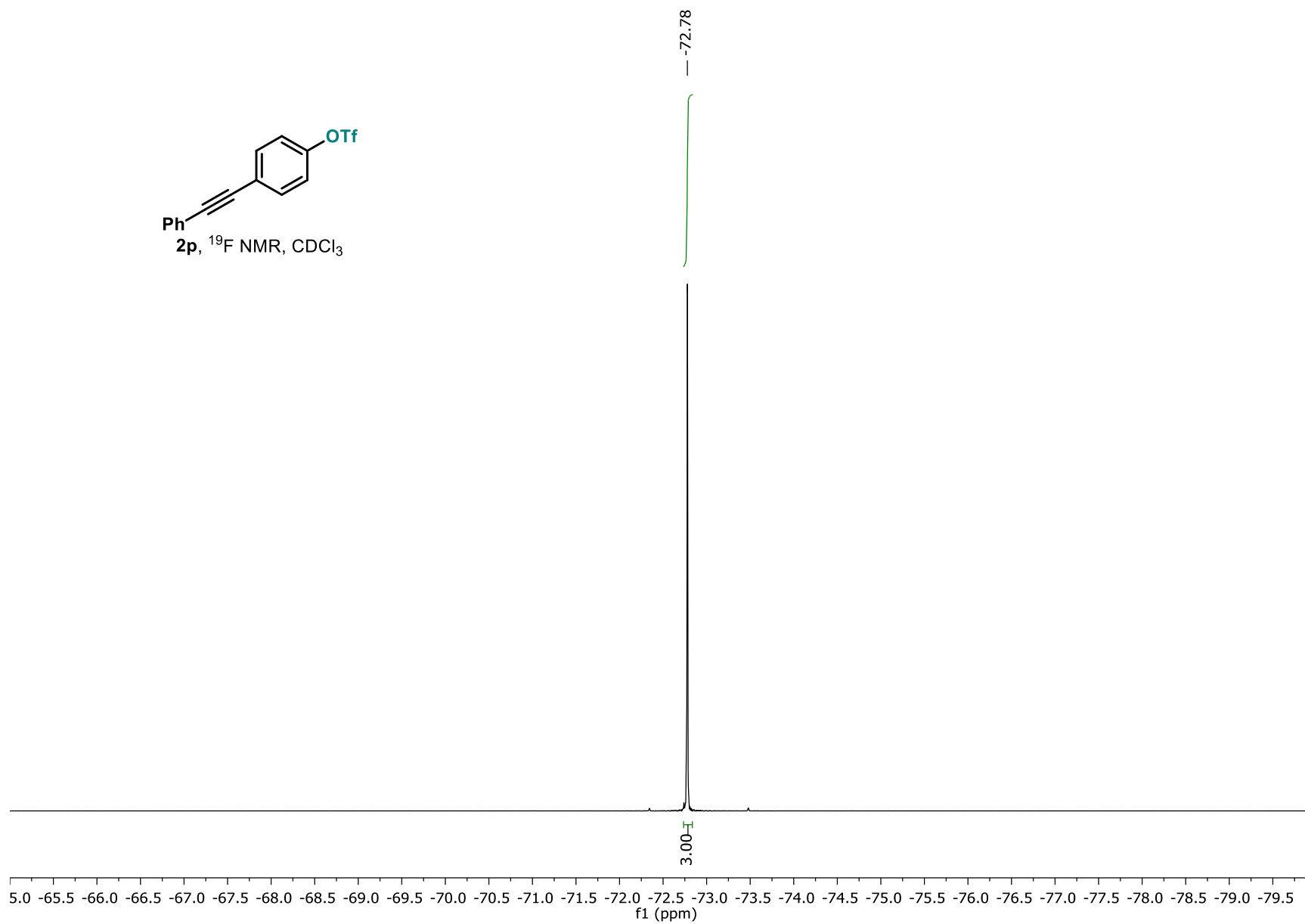
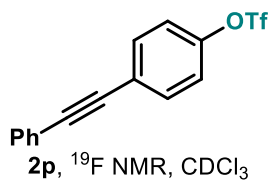


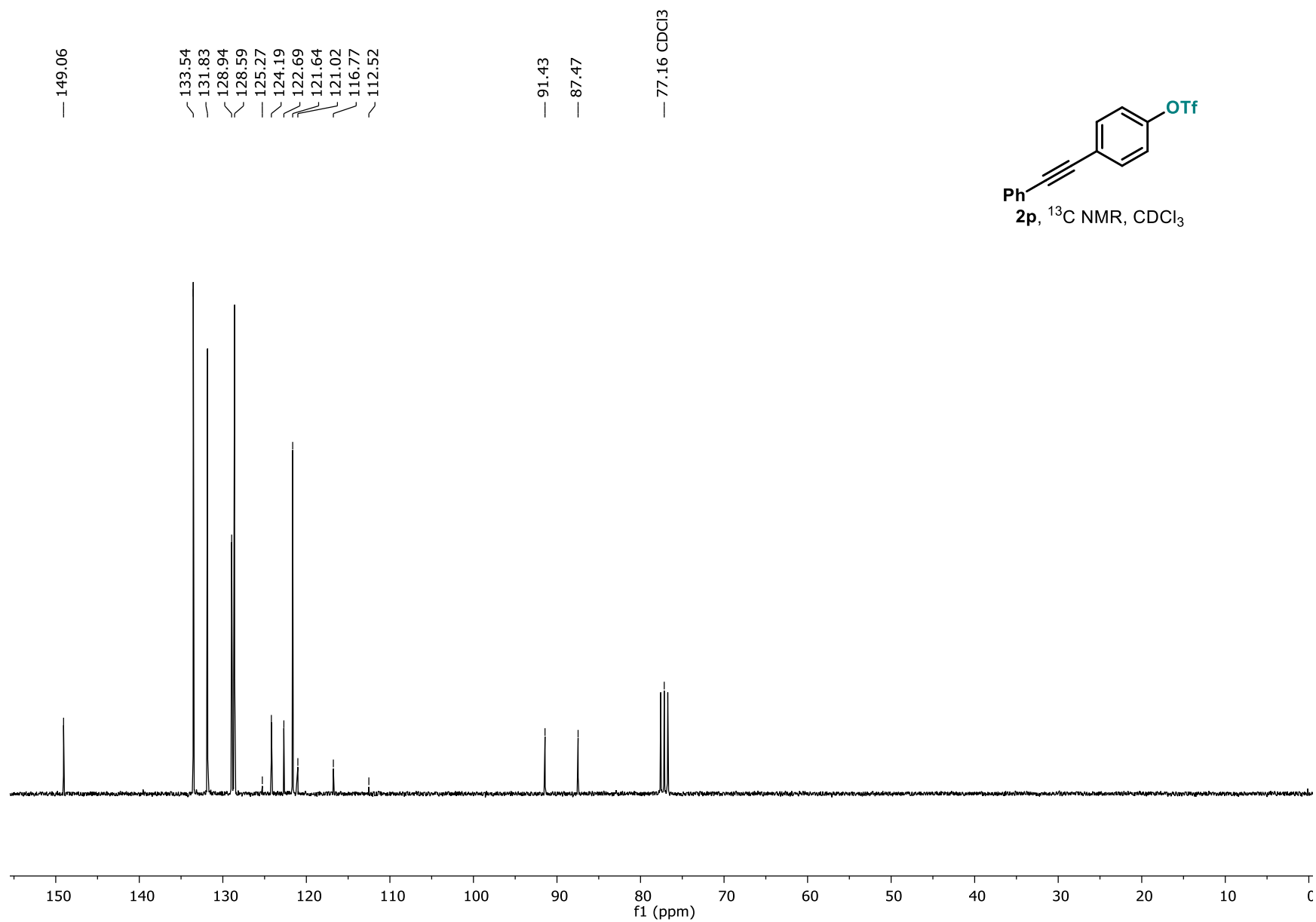


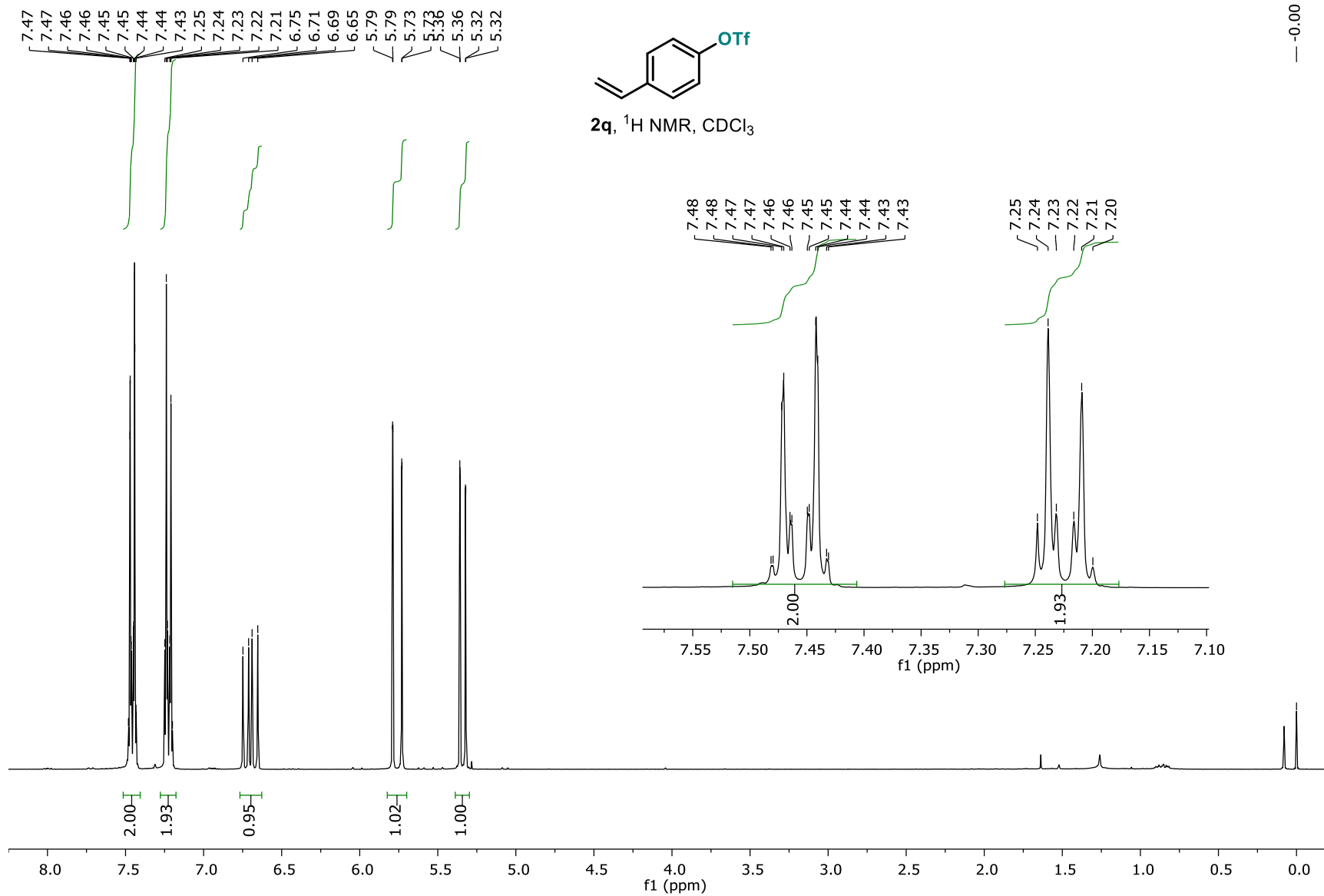


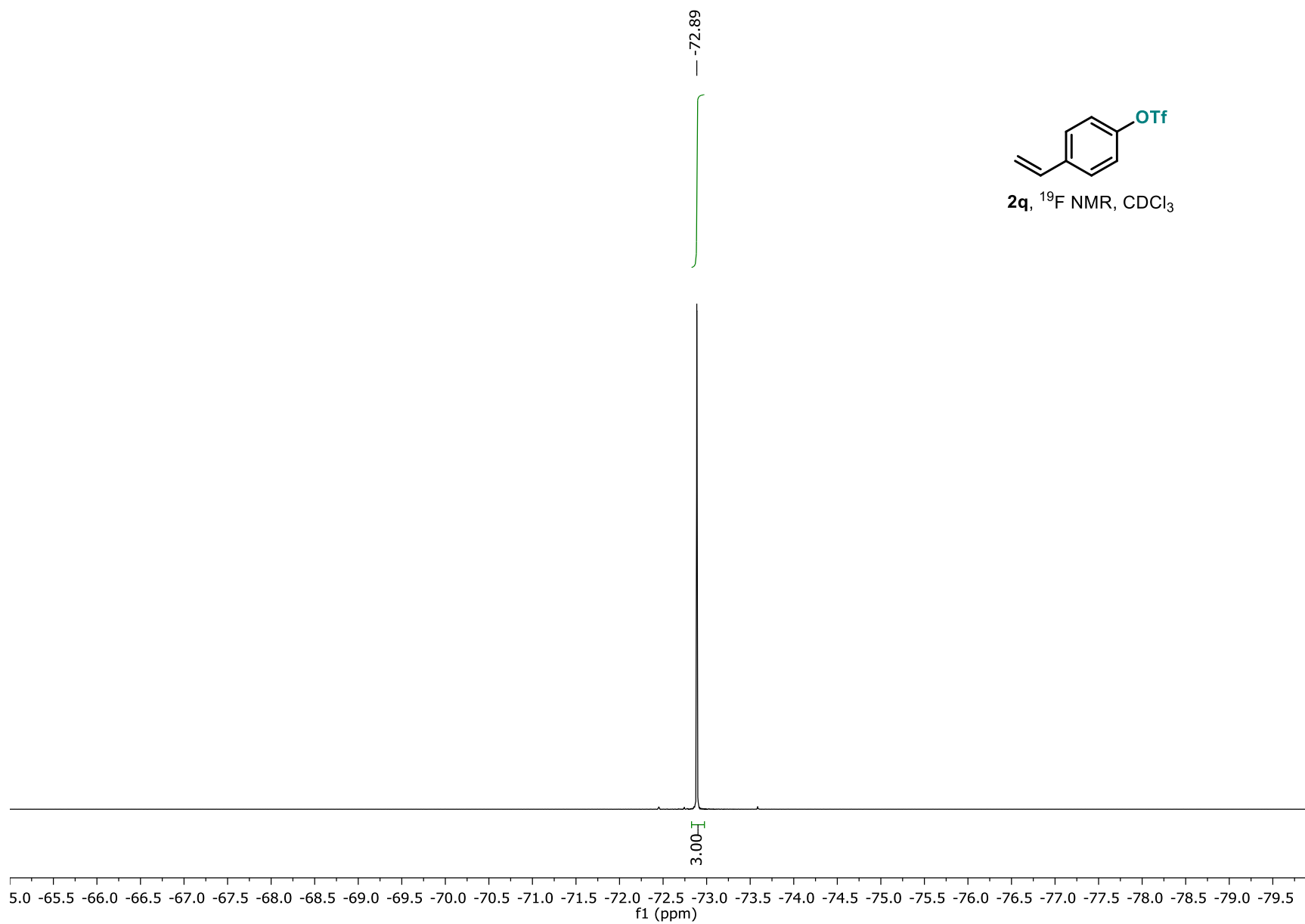


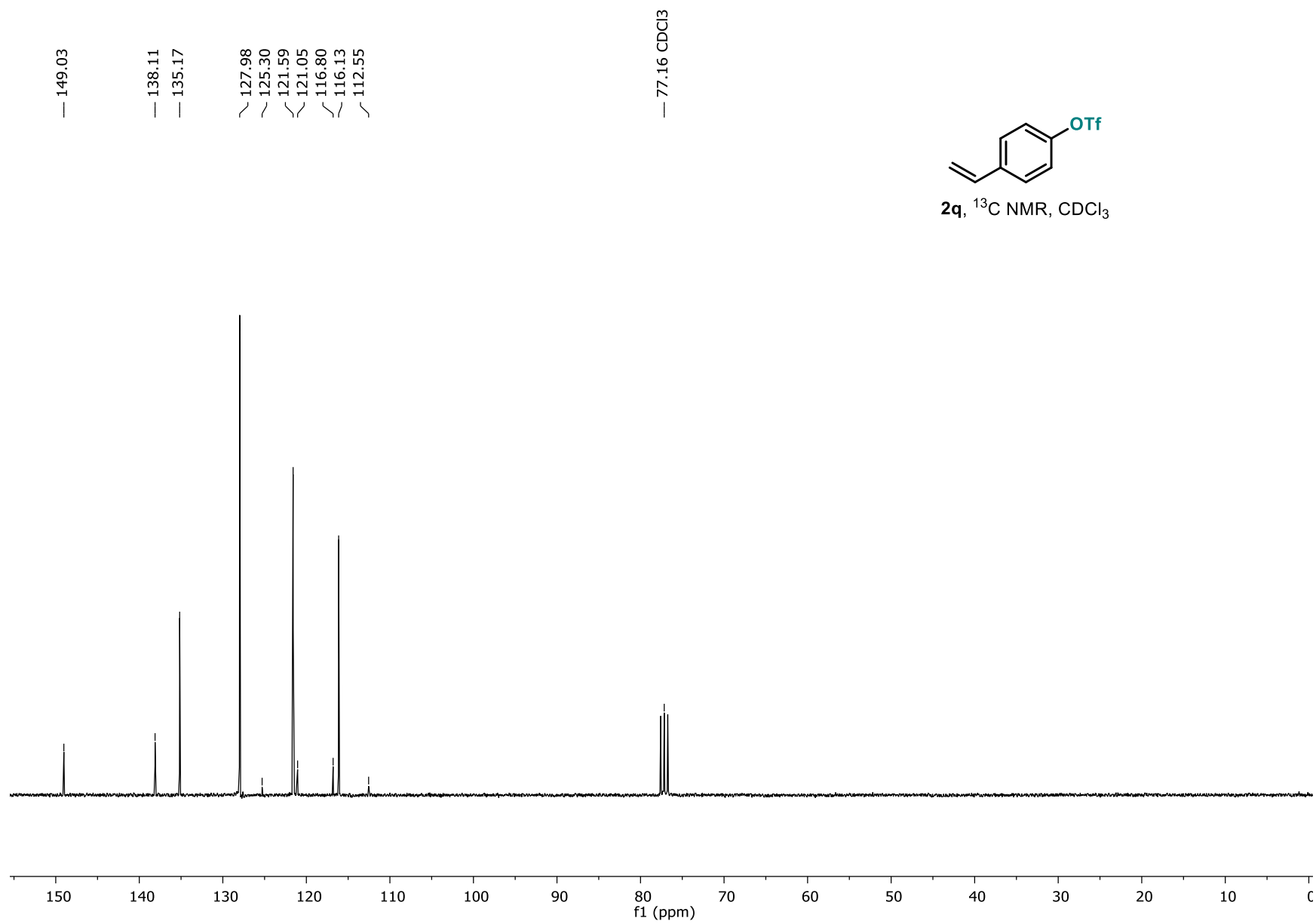


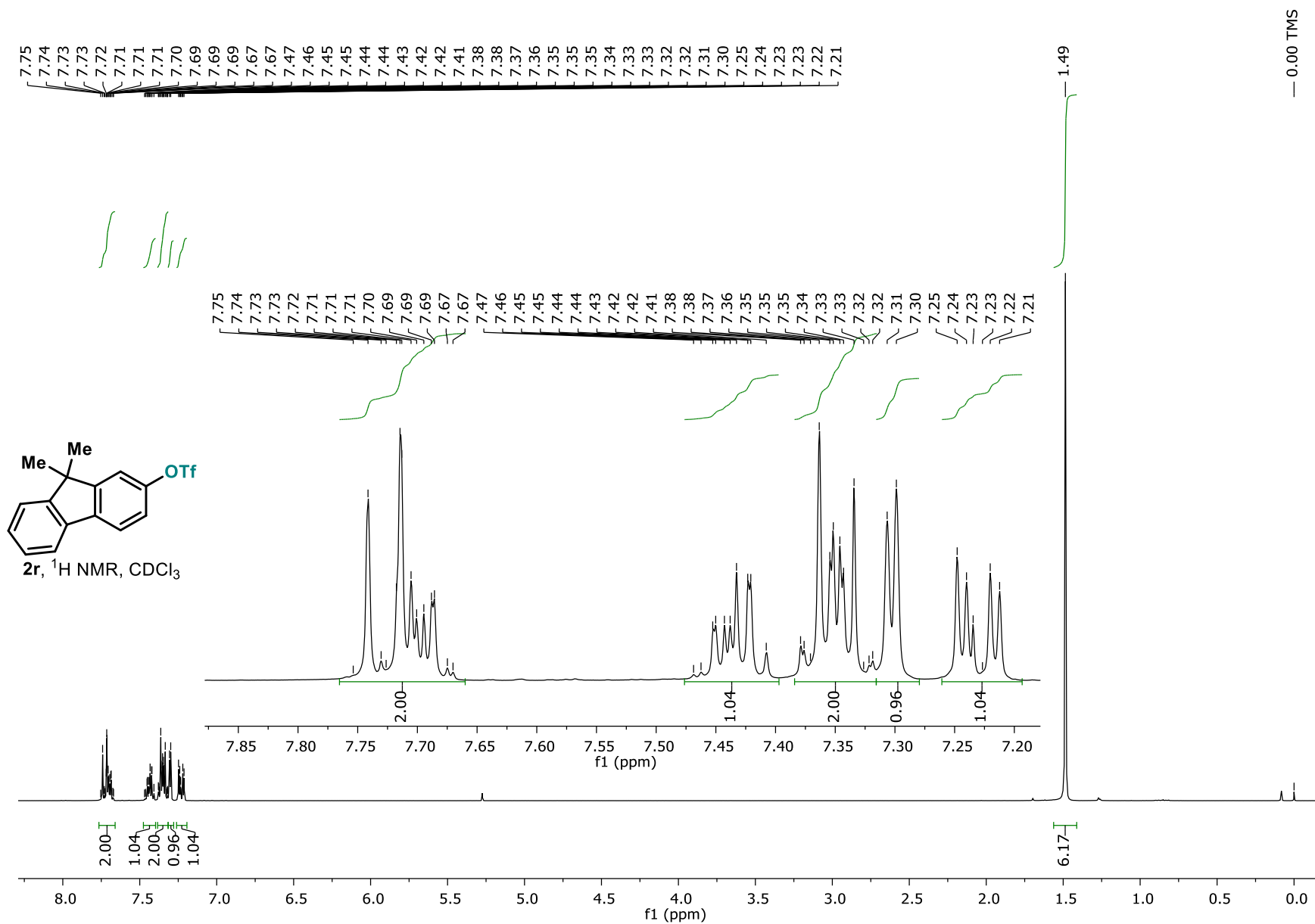




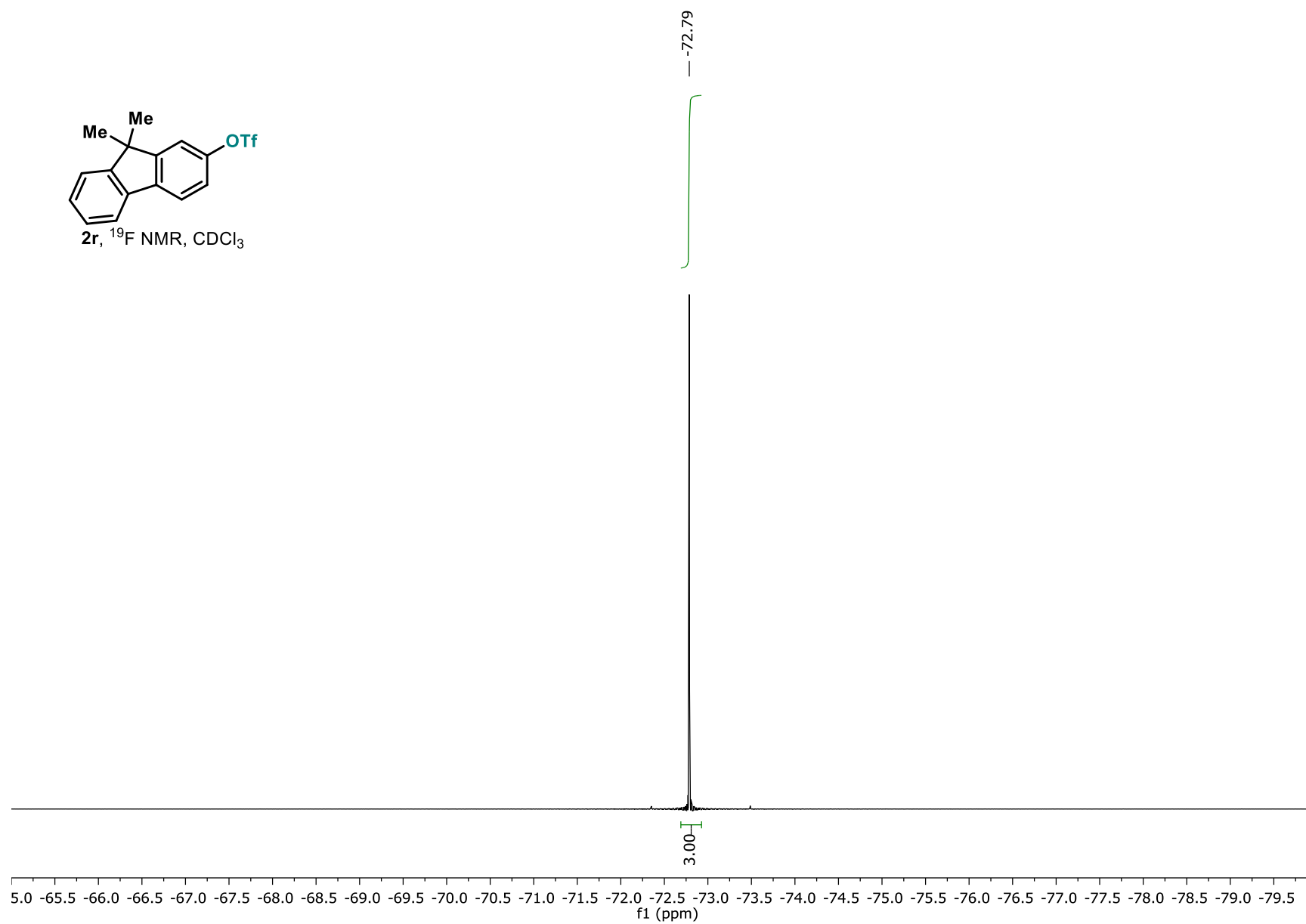
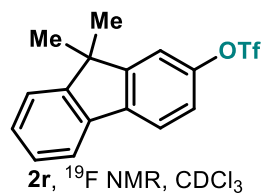


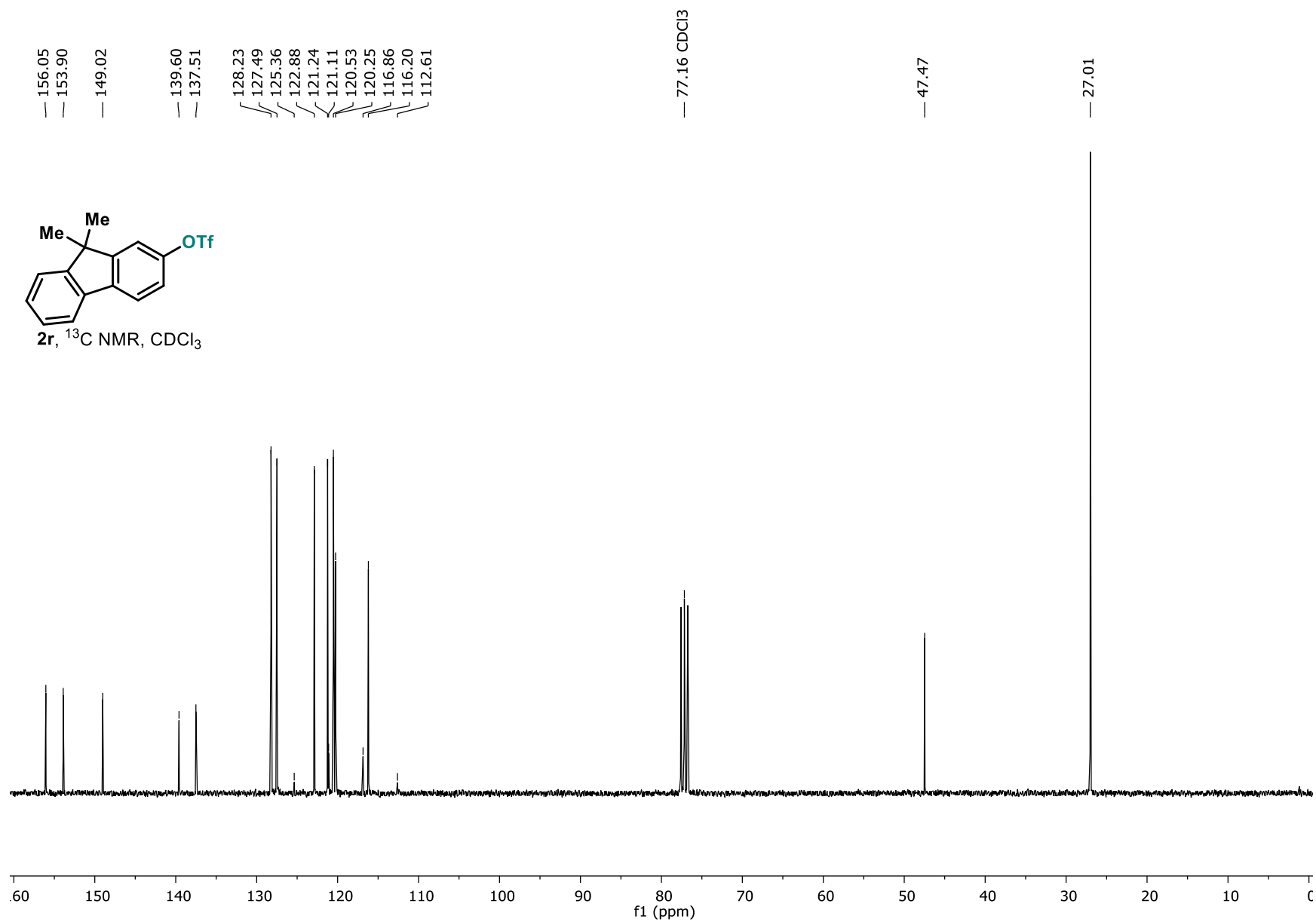




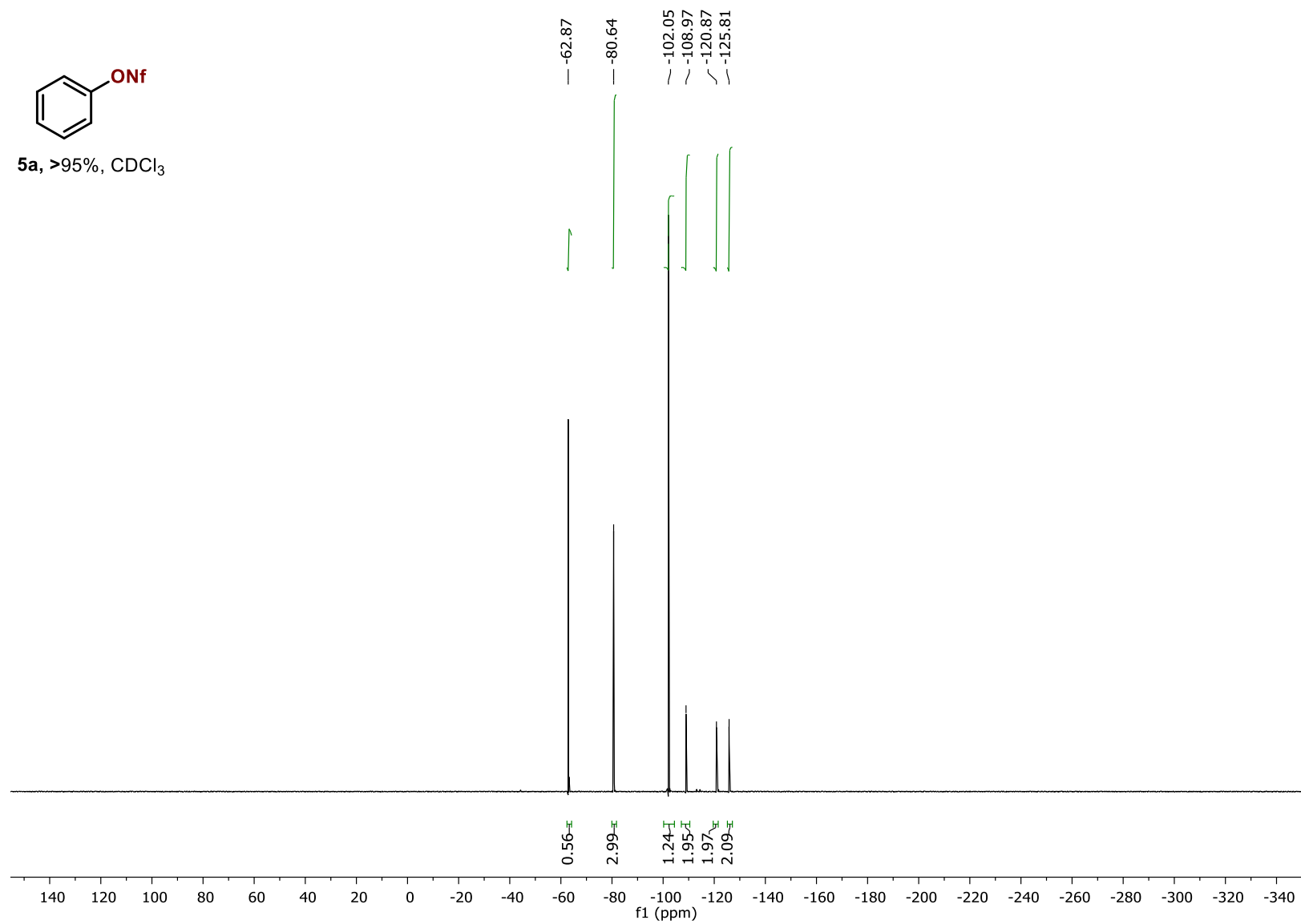


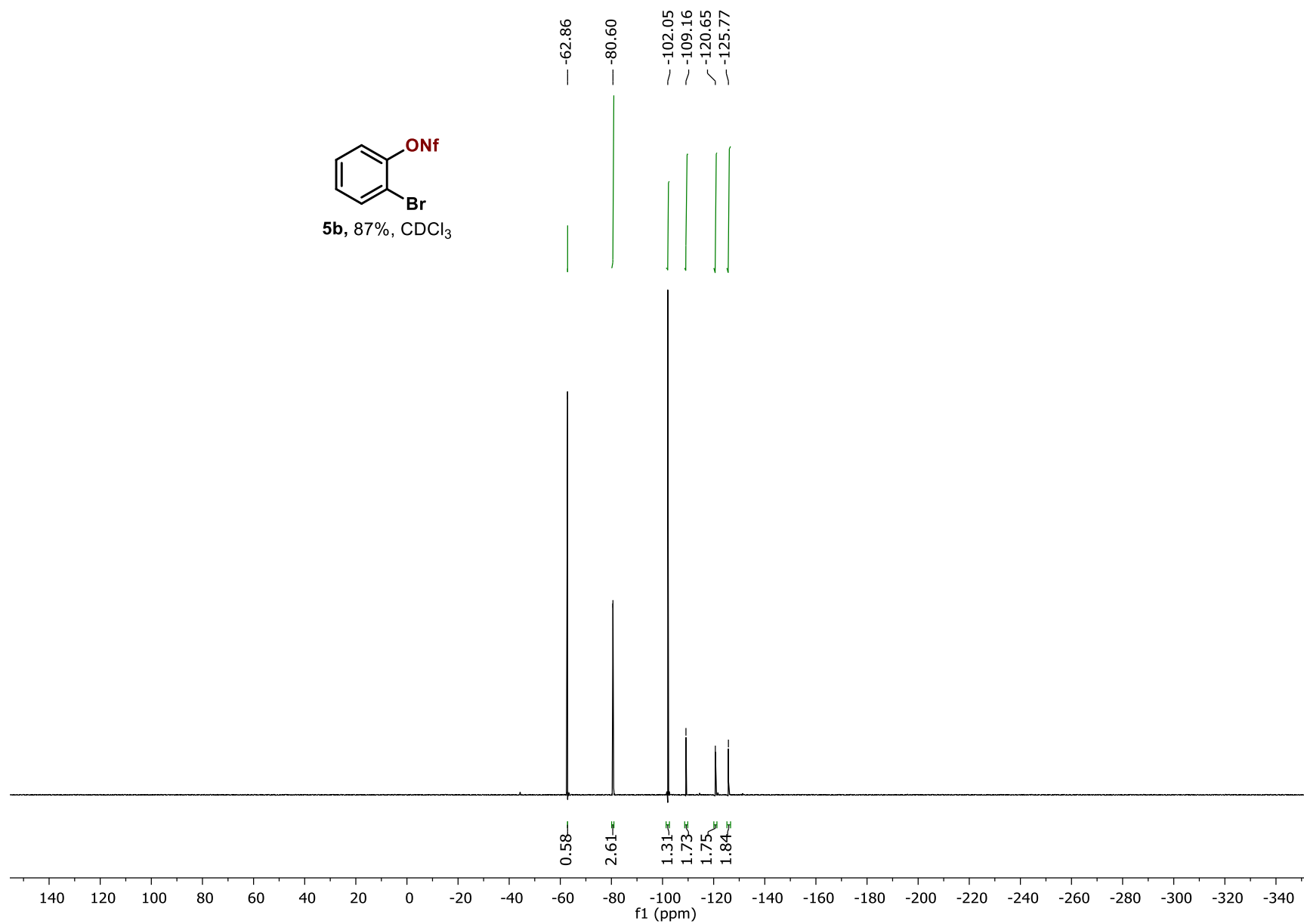
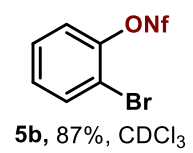


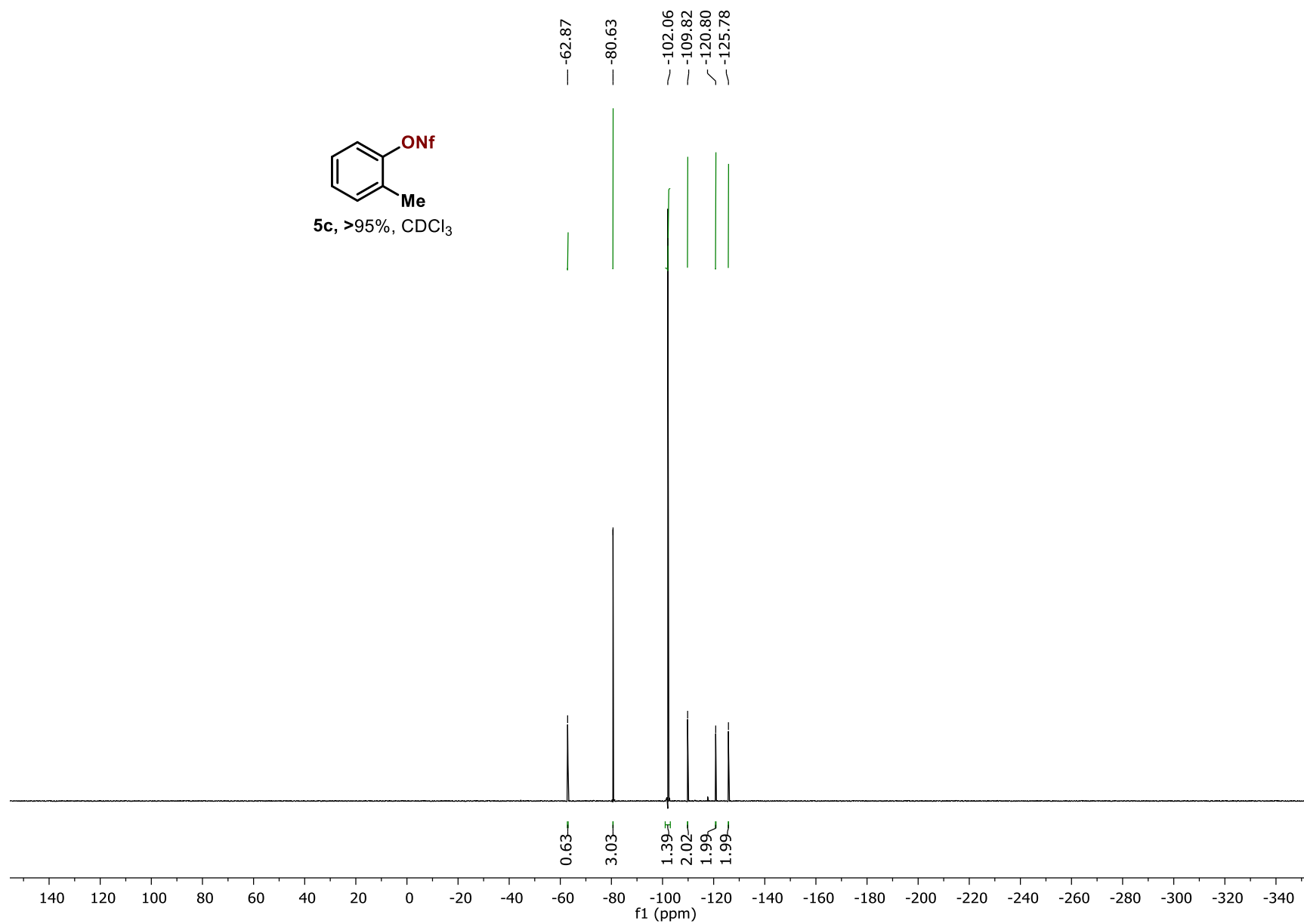
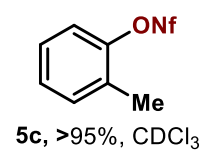


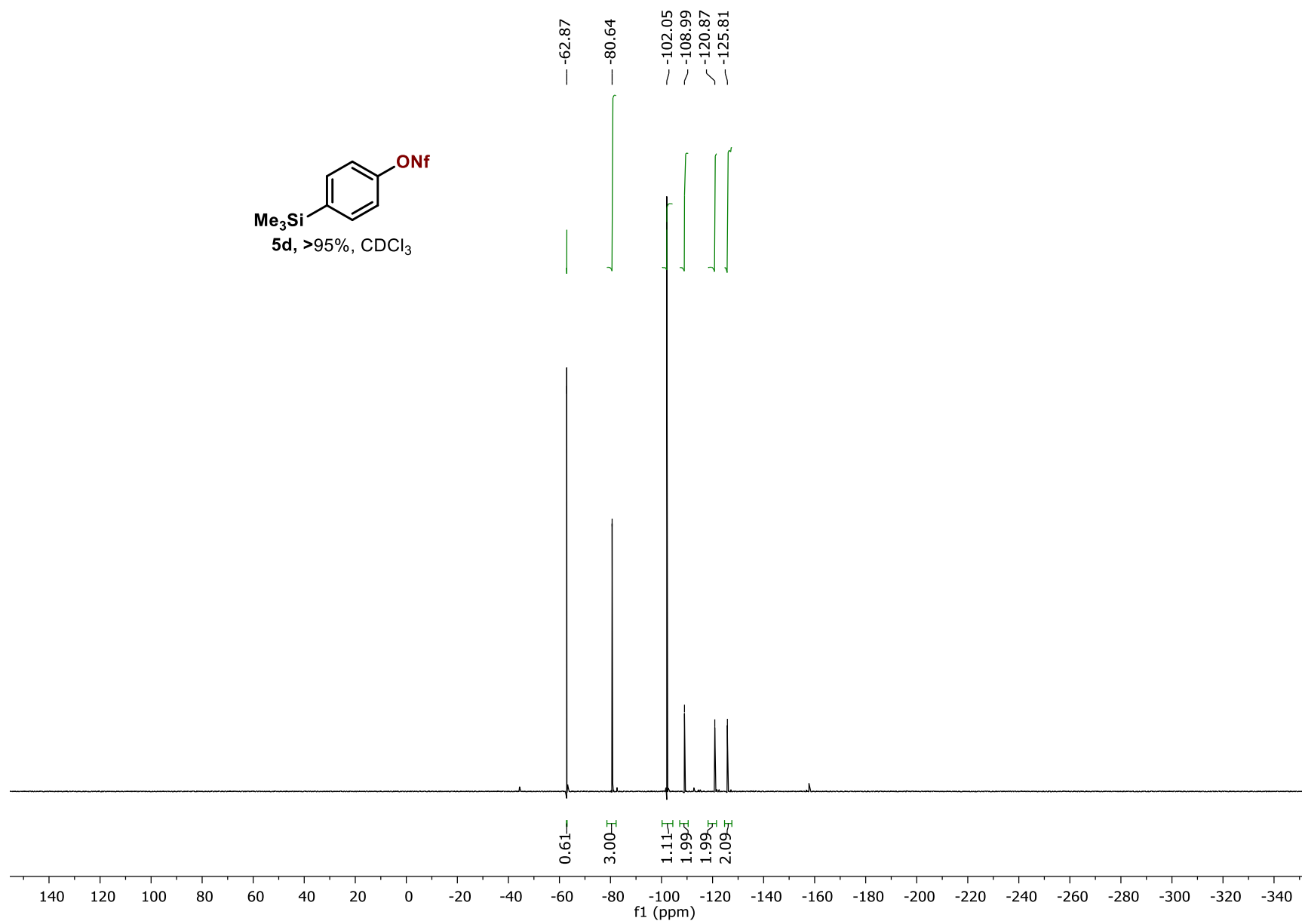
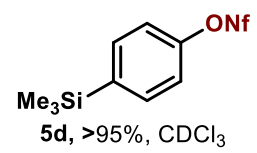


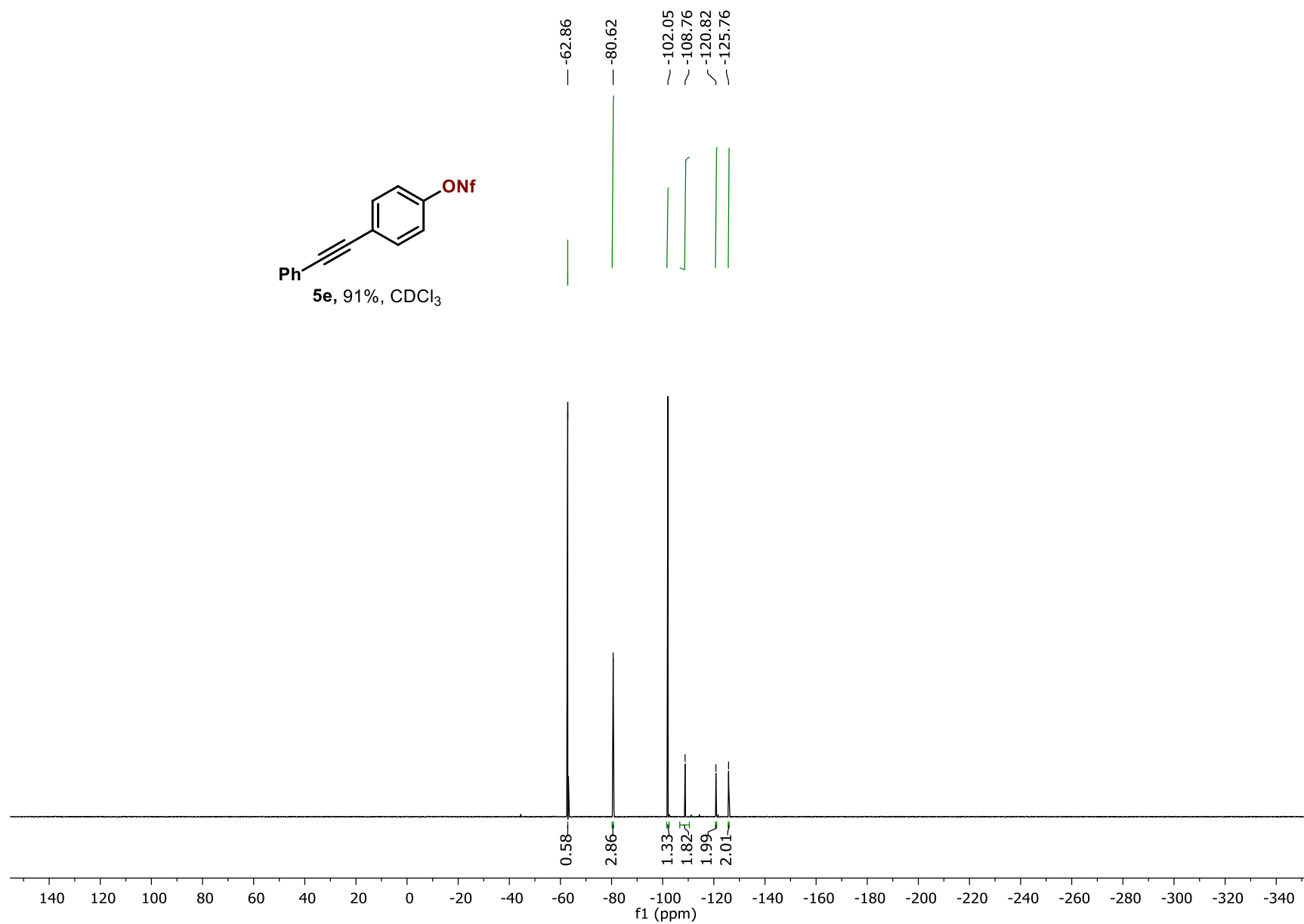
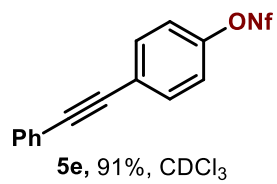
12.  $^{19}\text{F}$  NMR yields of the Bi-catalyzed coupling of arylboronic acids with KONf











### 13. NMR characterization of isolated aryl nonaflates 5

